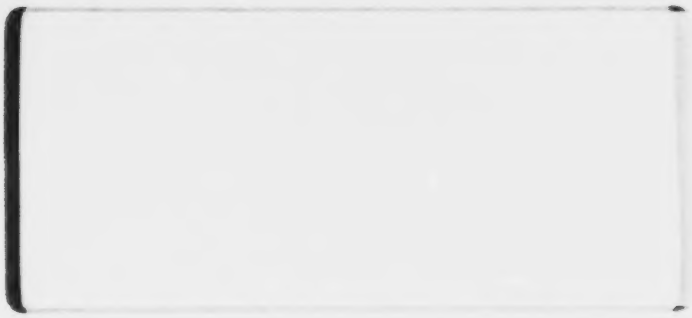

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HYDROGENATION AND ITS EFFECTS ON FLUID CATALYTIC CRACKING UNIT FEEDSTOCKS

Final Report

by

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SUMMARY

An experimental program was undertaken to quantitate the effects of hydrogenation on the cracking yields of conventional fluid catalytic cracking unit feeds. Results show increased yields of gasoline can be obtained from catalytic cracking by hydrogenating the feedstock.

Five gas oils from conventional and synthetic crude oils were hydrogenated over sulphided Ni/Mo and Ni/W catalysts at 343°C, pressures ranging from 2.76 to 13.78 MPa and LHSV of 1 or 2 h^{-1}. This produced a range of hydrotreated products which were catalytically cracked in a microactivity test apparatus to estimate fluid catalytic cracking unit yields.

Coker and conventional gas oils gave significant increases in gasoline yields (4-40%) after consuming 50-700 scf/bbl hydrogen. Synthetic gas oils from Syncrude and Suncor were much more difficult to hydrogenate, consumed less hydrogen (5-245 scf/bbl) and produced significantly less additional gasoline (4-9%) when cracked. Also, for all severely hydrogenated feeds, coke make was reduced significantly (17-43%).

Hydrogenation with the Ni/Mo catalyst at 13.78 MPa, 2 LHSV and 343°C produced the highest gasoline yielding feeds. As well, nitrogen and sulphur elimination were greatest at these conditions.

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OBJECTIVE

The broad objective of this project is to encourage the utilization of Canadian heavy oil and tar sand resources by means of developing improved methods or more economical schemes of refining synthetic crudes into liquid fuels.

The specific objectives of this project are

1. To evaluate the effect of hydrogenation on the quality of synthetic and conventional gas oils

2. To determine potential fluid catalytic cracking unit product yields by evaluating synthetic oils, conventional gas oils, and their hydrotreated products in a laboratory cracking apparatus (microactivity test).

3. To assess the benefits of hydrogenation and catalytic cracking of gas oils versus direct cracking and determine the extent to which hydrogenation and catalytic cracking can enhance liquid fuel yields.

JUSTIFICATION

To meet future Canadian demands for transportation fuels from a refinery diet composed of larger amounts of synthetic crudes, Canadian refiners will need to develop new and alternative upgrading technologies. Hydrogenation of synthetic crude and gas oil feedstocks presently charged to fluid catalytic cracking units (FCCU) offer such an opportunity since the addition of hydrogen to these materials has the potential to yield more liquid products and less coke (1). Conventional gas oils which are usually coprocessed with Syncrude materials will be affected in the same beneficial manner. By charging feedstocks which produce more liquids and less coke to fluid catalytic cracking units, refiners will have the opportunity to coprocess more residua since the unit will not be coke limited. Thus hydrogenation of synthetic and conventional crude oil FCCU feedstocks will have the potential of upgrading these materials both directly, by increasing liquid yield, and indirectly, by allowing more residua to be coprocessed.

BACKGROUND

The greatest proven Canadian reserves of hydrocarbons are the heavy oil and tar sands deposits of Western Canada. Commercial development of these resources has been limited to the Suncor and Syncrude tar sands plants of Alberta which are based on coking or carbon rejection technologies.

Heavy oil and tar sands represent young immature crude oils. Since their biogenesis is not complete, these materials are hydrogen deficient (low H/C ratio) and have very high concentrations of nitrogen, sulphur and metals (2). Upgrading such materials can be accomplished by either hydrogen addition or carbon rejection. The latter has generally been favoured by using delayed or fluid coking technology since, as well as rejecting carbon, nitrogen, sulphur and metals are eliminated at low cost. However, unlike hydrogenation, coking produces a relatively low yield of an unstable liquid product which is quite aromatic and refractory. Even when stabilized with some hydrogenation, coked products such as Syncrude gas oil are poor fluid catalytic cracking unit feedstocks. Syncrude and Suncor gas oils give both low conversion and coke yield, forming large quantities of cycle oils. These cycle oils are useful only in materials such as furnace oil since their high aromatic content makes their use in transportation fuels limited.

Conventional fluid catalytic cracking unit (FCCU) feedstocks are heavy distillates or gas oils with normal boiling ranges of 300 to 525°C. In areas where asphalt or bunker sales are limited, cokers have been installed to reject carbon from vacuum tower bottoms producing coker gas oils which, with mild hydrogenation, are used as FCCU feedstocks. With coker gas oils the degree of hydrogenation generally increases FCCU liquid yields and decreases the coke made.

The reduction of coke precursors in FCCU feedstocks should also allow the coprocessing of high coke precursor feeds such as residua. This will be particularly useful when such units are required to run at capacity since under such conditions resid cracking cannot be carried out in present units due either to metallurgical or blower limitations. Hydrotreating of Syncrude and

conventional gas oils may therefore enhance liquid yields directly for the gas oils and indirectly by allowing the residua to be processed at high capacity. As a result more liquid fuels will be derived from both the hydrotreated gas oil and the coprocessed residua.

EXPERIMENTAL

The experimental work carried out in this contract is subdivided into four sections:

1) Feedstock Preparation
2) Feedstock and Hydrogenated Product Characterization
3) Hydrogenation of Feedstocks
4) MAT Evaluation of Feedstocks and Hydrogenated Products

The following is a description of the experimental procedures used in this contract.

1) Feedstock Preparation

Five gas oils from synthetic and conventional sources were obtained for this study. The following is a list of the gas oils and the order in which they were hydrogenated:

1. Sour Gas Oil (G.O.) - Lloydminster Sour Blend
2. Sweet G.O. - Rainbow Zama
3. Syncrude G.O. - Syncrude Gas Oil
4. Suncor G.O. - Suncor Gas Oil
5. Raw Coker G.O. - Edmonton Coker Gas Oil

The Edmonton Rainbow Zama had a high final boiling point (622°C) and so was fractionated to bring the distillation range in line with the other gas oils of the study. The remaining four gas oils were analyzed and hydrogenated as received.

2) Feedstock and Hydrogenated Product Characterization

Fluid catalytic cracking feedstocks are characterized by a number of physical and compositional properties determined by generally accepted and standardized methods (3). The physical properties determined include: specific gravity, aniline point, viscosity, Conradson carbon content, as well as nitrogen, sulphur and metals concentrations and normal boiling range.

Specific gravities for all materials were determined in a Paar Densitometer at specific temperatures such that the material was a liquid. The densitometer measures specific gravity on the basis of an oscillating tube filled with liquid. Specific methodology is

outlined in ASTM Method D4052-81. The specific gravity, once determined, can be converted to the API gravity by the following relationship:

$$°API = (141.5/s.g \ @ \ 60°F) - 131.5$$

Specific gravity increases or API gravity decreased with increased residua content and/or aromatic content in a feedstock.

Aniline point is another standard ASTM method (D611) which measures the temperature of miscibility of aniline with an equal volume of liquid hydrocarbon sample. The aniline point is a rough measure of the paraffin content of the sample since it increases with paraffin concentrations, assuming all factors such as molecular weight and boiling range are equal.

The viscosity for all feeds was measured with a Zeitfuch pipette at 100°C. Viscosity increases with the molecular weight and the boiling range of the material analyzed. This method is also a standard industry procedure outlined in ASTM D445.

The Conradson carbon determination is used to measure a material's propensity for forming coke. The experimental procedure employed was a modification of ASTM D189 in that an Alcor MiniConradson carbon analyzer was used. This instrument produces superior results because it employs both a nitrogen gas blanket and an automatic programmed temperature profile. As a result, analytical data is both more precise and reproducible.

Metals analyses, particularly nickel and vanadium, are another very important factor in assessing FCCU feedstocks. The metals are found in all crude oils, generally as prophyrin complexes, and because they are high molecular weight species they occur in the gas oil and particularly the residual fractions. Feedstocks are analyzed for metals by combustion in a platinum dish followed by washing the combustion residue with isooctane onto a Millipore filter. The filter cake is then sandwiched in a plastic cell and metals are determined by X-ray fluorescence.

Gravity, aniline point, viscosity, Conradson carbon residue, when taken together and compared with other similar feedstocks, are an indication of the refractory nature or heaviness of the feedstock.

In elemental terms, the heavier a feedstock becomes, the more hydrogen deficient it becomes and as a result gravity, viscosity and Conradson carbon residue increase.

Nitrogen and sulphur levels are important variables in fluid catalytic cracking due to their effect on catalysts, product quality and stack gas emissions from the regenerator and associated boiler. High nitrogen contents in FCCU feeds, in excess of 1000 ppm, have been known to cause catalysts to lose activity. This has generally been attributed to basic nitrogen compounds which bind to Lewis acid sites during cracking, causing the loss in activity. High sulphur contents are also deleterious to product quality, since the significant amounts of sulphur contaminate FCCU liquid products. More importantly, organic sulphur and nitrogen are oxidized in the regenerator to form their respective oxides, which can present the refiner with pollution problems. Since the sulphur levels in most feedstocks are an order of magnitude greater than nitrogen levels, they present the greatest pollution problem. For the materials evaluated in this work, sulphur has been determined by X-ray fluorescence with a PGT-100 instrument, while nitrogen has been analyzed by a microcoulometric method.

All feedstocks and hydrogenated products were analyzed for normal boiling range by a gas chromatographic simulated distillation, as described in ASTM D2887. The method consists of injecting a liquid sample into a temperature programmable gas chromatograph equipped with an 18" x 1/4" dia. 10% OV-101/Chromasorb P column and an FID detector. The instrument is calibrated for retention time and true boiling point with a blend of n-paraffins which cover the boiling range of the sample to be determined. The instrument produces a chromatogram whose area slices are summed and normalized with respect to the total area to report a true boiling point curve for distillates on a mass% basis. For residua the technique is modified to include an internal standard, since all of the sample will not elute due to its low vapour pressure. Residua are defined in terms of normal boiling point and are typically that portion which has a normal boiling point greater than 504°C.

Compositional analyses were obtained by mass spectrometry in conjunction with both column chromatography and/or distillation. Compositional analyses of some feedstocks and hydrogenated products (i.e. Syncrude and Suncor) required fractionation, column

chromatography and mass spectral analysis due to their lower initial boiling points. Most feedstocks and products were evaluated using column chromatography and mass spectral analysis.

The samples were separated into saturate, aromatic and polar fractions on a tripart clay/silica gel/alumina column. Elution of the sample with hexane allowed the saturates to be collected at the bottom of the column while the polar and aromatic fractions were adsorbed on the clay and silica gel adsorbents, respectively. Both aromatic and polar fractions were eluted with diethyl ether and methanol. Evaporation of the solvents left saturate, aromatic and polar fractions. The former two fractions were analyzed separately on a Kratos 25Q mass spectrometer and the results, when combined with elution chromatography data, allowed the complete composition of the gas oil to be reported.

3) Hydrogenation of Feedstocks

Hydrogenation of the gas oil feedstocks was carried out at the Gulf R&D Pilot Plant using the P-15 hydrotreating reactor (Figure 3-1).

The P-15 is a down flow, fixed bed hydrotreater with a once-through gas design. The reactor is equipped with feedstock and hydrogen metering devices, as well as a nitrogen purged product collection vessel to remove H_2S from the liquid effluent.

The reactor system is composed of an inline feedstock preheater followed by a reactor vessel heated along its length by external resistance heating. The reactor effluent is passed through a heat exchanger to a separator to remove reaction gas. Temperatures are controlled by feedback type controllers and the pressure is controlled by a back pressure relief system.

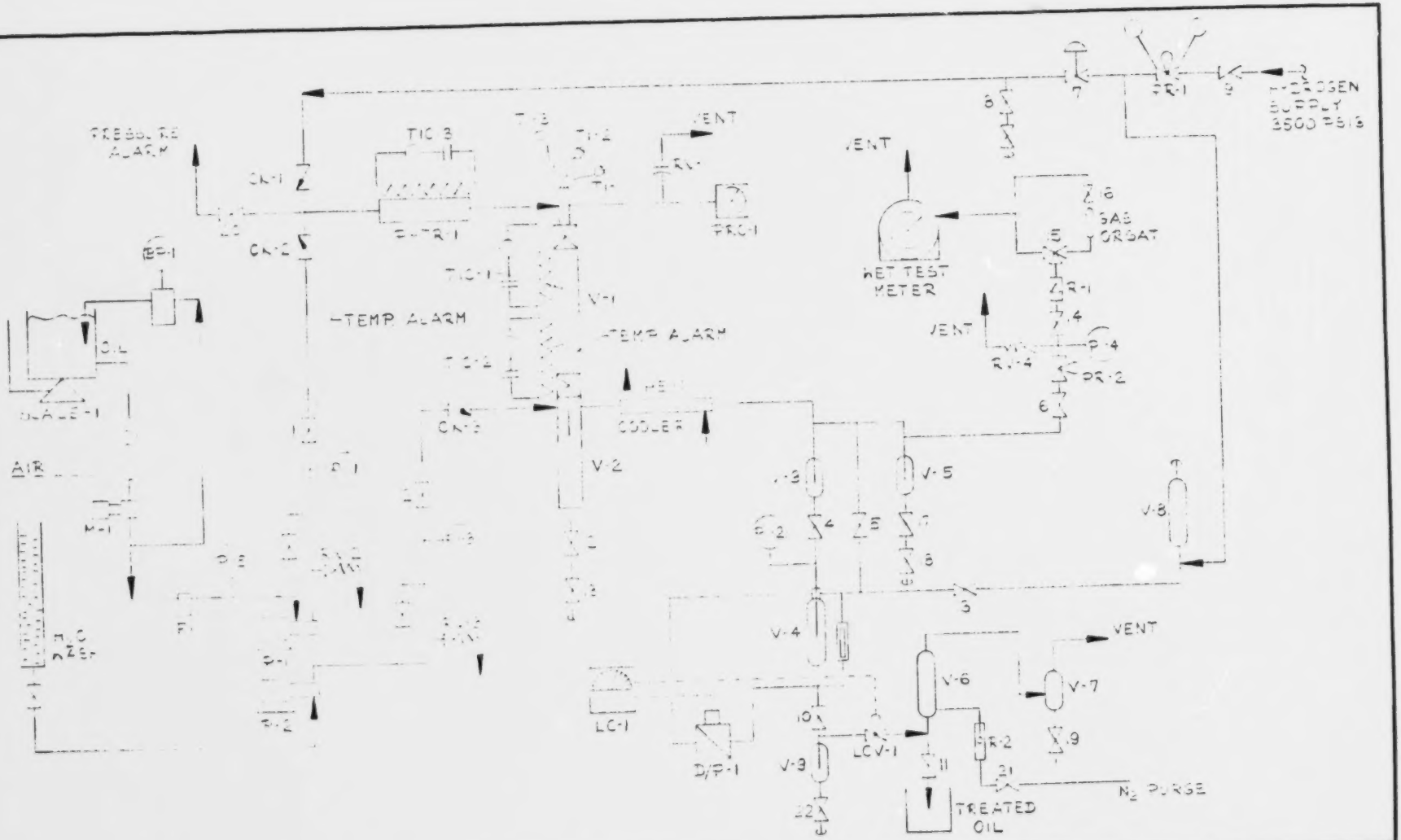
All five gas oils were hydrogenated under four reaction conditions using two different catalysts:

	Quantity	Catalyst	Metal Composition
1st Catalyst	150 mL	NT-550	4% Ni 16% W
2nd Catalyst	150 mL	NM-506	.5% Ni 18% Mo

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

Note: Reactor temperature was increased from the contract temperature of 288°C to give maximum desulphurization and denitrogenation with a minimum of thermal cracking.

FIGURE 3-1



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PROJ NO.

GULF CANADA LIMITED
RESEARCH AND DEVELOPMENT DEPARTMENT

P-15 HYDROTREATER
FLOWSHEET
PILOT PLANT

CLASS NO
DATE APRIL 85
SCALE NONE
DRAWING NO B-2265-RD-1

Each hydrogenation run consisted of the following steps:

1. Set the necessary reaction condition for the reactor.

2. Line out the reactor for 8 hours (12 hours for reaction condition #4).

3. Take 2 x 2-hour samples (3 x 2-hour samples for reaction condition #4) for a given reaction condition.

4. Check log book for stable pressure, temperature and feed rate during line out and sampling.

5. Steam heat sample and nitrogen purge for approximately 30 minutes to remove all traces of H_2S.

6. Analyze individual 2-hour samples for density, % sulphur and hydrogen content.

7. Combine identical 2-hour samples and submit product for complete physical analysis.

8. Set the next reaction condition for the reactor.

After all four reaction conditions had been run for a given feed, the reactor was flushed for 8 hours with a toluene/light distillate solvent to remove all traces of previous feed from the catalyst.

In order to monitor any activity change in the hydrogenation catalysts during the study a "standard" (Lloydminster Sour Blend D85-8-1 Reaction condition #3) was run at the beginning, middle and end of the series of runs for each catalyst.

4) MAT Evaluation of Feedstocks and Hydrogenated Products

The microactivity test (MAT) was the primary experimental method used in this work. The procedure employed was a modification of ASTM D3907-80, which is a standard method evaluating FCCU catalyst activity. In the ASTM method, the gasoline yield (IBP-216°C) of a specified feed is determined under a standard set of conditions (T = 482°C, C/O = 4). The procedure was modified so that reactor temperature, hydrocarbon feedstock, and the ratio of catalyst to

oil can be varied. The total MAT product range - gases, liquids and coke on spent catalyst - was determined so that a complete product yield for the MAT experiment could be calculated. These products included hydrogen, methane, LPGs, gasolines (C_5 - 220°C), light cycle oil (220-344°C), decant oil (344+°C) and coke and since they were evaluated, their yield as a function of MAT operating conditions is known.

The MAT is a fixed bed downflow reactor constantly swept by an inert gas (nitrogen) during the course of the experiment. While it is operationally quite different than a commercial riser/cracker, experience and the literature (4) has shown that the directional changes in operating conditions in both units are reflected in similar changes in product yields.

A schematic diagram of the experimental apparatus is shown in Figure 4-1 and the procedure for operating this unit follows. A MAT reactor is a 40 cm long x 1.2 cm O.D. tubular reactor equipped with a constriction in the middle of the tube, a male B-14 ground glass joint on the reactor bottom and a septum port and a side arm for charging feed and gas to the reactor at the top. A glass wool plug is placed above the constriction and the desired amount of catalyst to be studied is weighed by difference into the reactor. A second glass wool plug is placed on top of the catalyst and sufficient 3 mm glass beads are placed on top of this plug to fill the reactor to within 5 cm of the septum. A septum cap is put into the septum port and for this study one J-type thermocouple was attached to the outer skin of the reactor to measure skin temperature at the top of the catalyst bed. With longer catalyst beds a second thermocouple can be used to measure mid point temperatures of the bed.

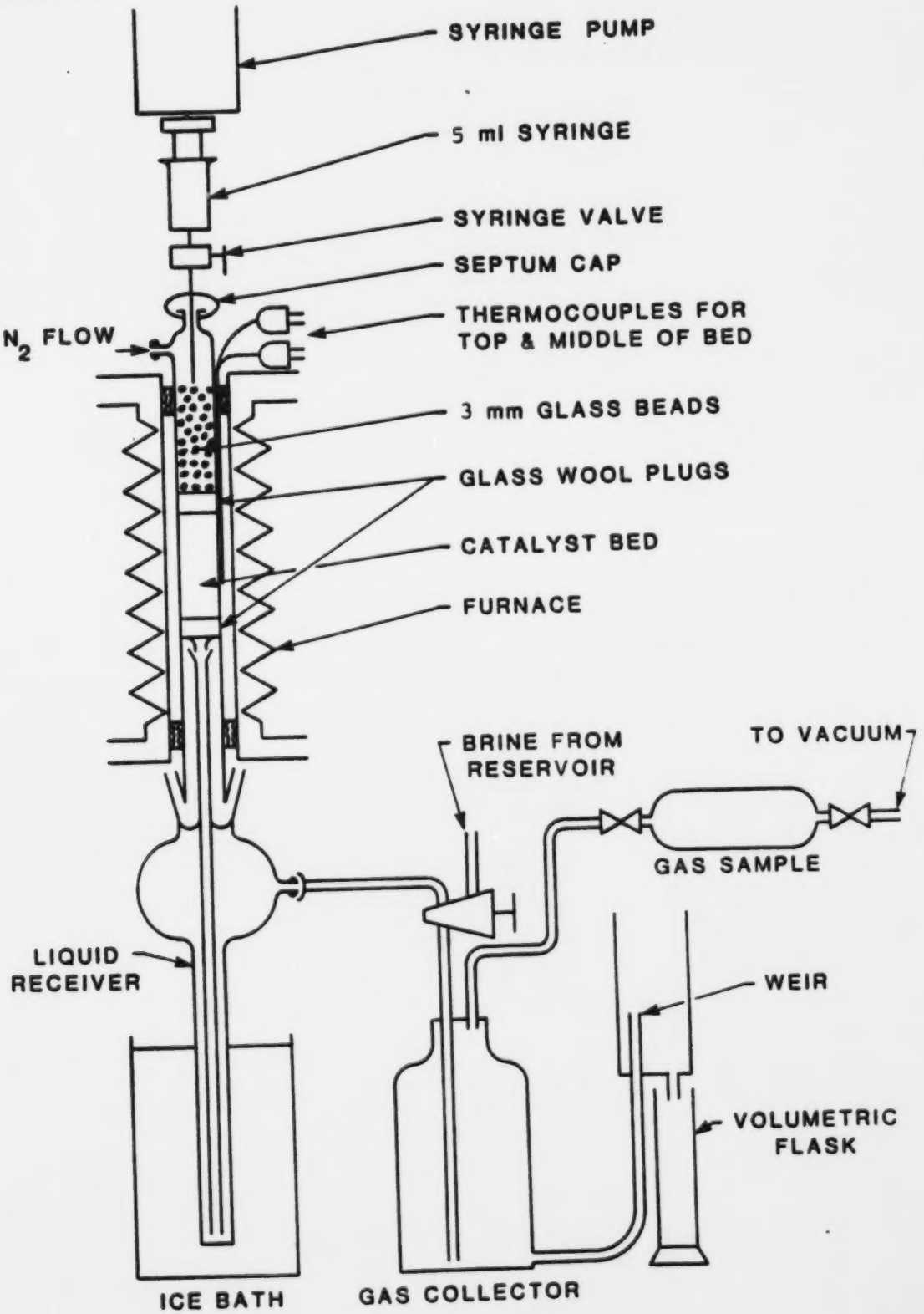
The reactor is then placed in a vertical tube furnace and a nitrogen line is attached such that the flow of gas through the reactor is maintained at 20 mL/min. A manometer is also attached to the incoming gas line so that the differential pressure across the bed can be measured. The reactor is then heated to reaction temperature and a preweighed liquid receiver is connected to the bottom of the tubular reactor. The liquid receiver is immersed in an ice bath and vented through 4 mm O.D. nylon tubing to a gas collection system which has the ability to contain the entire gas stream

evolved during the course of the experiment. Once the reactor has reached thermal equilibrium at the desired temperature, the nitrogen flow rate through the bed is adjusted to exactly 20 mL/min and the temperatures at the top and the middle of the bed as well as the ambient temperature are recorded along with the pressure differential across the reactor and the barometric pressure.

The hydrocarbon feedstock to be tested is charged to a hypodermic syringe. Care is taken to exclude air and the syringe with the approximately 1.1 mL of feed is weighed. It is then injected through the septum cap and the syringe pump is connected with the barrel of the syringe to begin pumping feed. When ready, the operator begins injecting feed by starting the syringe pump and timer. Simultaneously, the gas flow from the liquid receiver is diverted to a gas collection bottle. The brine in the bottle is displaced over a weir which is adjusted so that the collected gas is at ambient temperature and pressure. The displaced brine is collected in a 1000 mL graduated cylinder so that the total volume of gas collected can be measured. Approximately 1 mL of feed is injected over the first 100 seconds of the run. At that time, the syringe pump is stopped and the nitrogen flow is continued for another 800 seconds to strip both the reactor of liquids and the receiver of light petroleum gases. During the initial stages of the run, the maximum pressure across the MAT reactor, as well as the minimum flow rate and skin temperatures of the top and middle of the reactor bed are recorded. When convenient, the syringe is removed from the apparatus and weighed.

At the end of the 900 seconds, the MAT run is complete. The gas collection system is isolated, the furnace is shut off and the liquid receiver is removed from the apparatus, dried and weighed. The liquid in the receiver is then made as homogeneous as possible and transferred to a liquid capsule bottle which is refrigerated. The liquid material is eventually analyzed by a gas chromatographic simulated distillation, as described above under Feedstock Evaluation, in order to determine the fractions of reactor effluent liquid which have boiling points of 220°C and 344°C. The total volume of brine displaced is recorded and a composite sample of the collected gas is taken with an evacuated Orsat bottle. The gas composition is then determined by mass spectrometry on an MS5 instrument. Once the reactor cools to room temperature under a flow of nitrogen, it is removed from the apparatus and the catalyst is recovered and analyzed for total carbon content. This completes the microactivity test.

Figure 4-1



A SCHEMATIC DIAGRAM OF THE MICROACTIVITY TEST APPARATUS

5) Microactivity Test Data Reduction

The microactivity test (MAT) can give a wealth of product yield data provided the gas, liquid and solids produced during the MAT run are analyzed in sufficient detail. Furthermore, the reliability of the data obtained must be verified by closing a mass balance around the actual experimental run.

Mass balances are calculated by comparing the weight of products to that of the feed injected. The weight of injected feed is determined experimentally from the difference in the weight of the syringe before and after injection. The weight of coke is determined directly from the weight of catalyst and its carbon content before and after the MAT run. The weight of liquid generated is also determined directly from the differences in liquid receiver weight at the end and the beginning of the experiment. The direct determination of weight of gas evolved can be made from the effluent gas composition corrected for air, water vapour and nitrogen content and the ideal gas law since the volume, pressure and temperature of the collected gas are known. When the directly determined weights of coke, liquid and gas are summed and compared with the weight of the feed injected, a mass balance expressed as a percentage of feed can be quoted. Acceptable MAT data have mass balances in the 97-102% range. Balances in the range of 95-105% may be acceptable if the feed or the catalyst is particularly troublesome.
Since the directly determined weights of products do not necessarily equal the weight of feed, MAT product yields are made whole by assuming any discrepancies in the data are due to errors in the amount of gas determined. This results in the weight of gas being corrected in order to force a mass balance and, therefore, the relative amounts of each of the gas components are adjusted accordingly. Gasoline yields are calculated from the C_5+ gasoline components and the weight of reactor effluent liquid which boils up to 220°C. Cycle oil yields are calculated directly from GCD data and the weight of the reactor effluent. These data are all reported on a mass% basis which is atypical with most of the data reported in the literature, particularly that from commercial operations which is reported in liquid volume%. Due to the very small samples of materials collected and the fact that they are not fractionated into products, densities cannot be measured and accurate volumetric yield reported. However, the data can be converted to such yields

if one is willing to assume average specific gravities for various materials. This should be done with caution.

The product yields are reported as a mass% of the feed and were calculated with the following expression:

yield ith product = (weight ith product/weight feed) x 100

RESULTS AND DISCUSSION

The primary purpose of this work was to evaluate the effect of gas oil hydrogenation on their catalytically cracked product yield. The uptake of hydrogen by these materials increased the concentration of gasoline precursors while reducing coke, decant oil precursors, poisons (i.e. Nitrogen, Nickel, Vanadium) and pollutants (i.e. Sulphur). Two hydrogenation catalysts were studied, one a sulphided nickel-tungsten type on an alumina base (NT-550) and the other a sulphided nickel-molybdenum type on an alumina base (NM-506). These catalysts were chosen for this study because of previous experience and favourable evaluations for upgrading Syncrude middle distillates in previous work (Ref 5).

The hydrogenation of the five gas oil feeds studied was done at four severities for each catalyst. This generated samples of the original and eight hydrogenated products for each gas oil studied. Complete physical and compositional data were determined for these materials, as well, MAT cracking yields with DA-250 catalyst at 490°C and a catalyst to oil ratio of 4. Data for each feedstock and its hydrogenated products are listed in a set of four tables (physical properties, boiling range, composition and MAT yields).

Selected properties such as sulphur content, nitrogen content, composition and MAT yields have been plotted against (calculated) Hydrogen Consumption to graphically show the effects of increased hydrogenation and help determine the superior catalyst.

1. Lloydminster Gas Oil

Feed Evaluation

Feedstock data given in Table 1 show Lloydminster gas oil was 21.6° API gravity feed with 2.0 wt.% sulphur, 0.049 wt.% nitrogen, 0.05 ppm nickel and 0.18 ppm vanadium. The aniline point of 66.1°C reflected the aromatic content of the gas oil.

Coke forming tendency as measured by Conradson Carbon was 0.09 wt.%. The boiling range, determined by gas chromatography and shown in Table 2, had a 307°C 5% point and a 466°C 90% point, which are typical for full range gas oils. The compositional analysis by Mass Spectrometry (Table 3) indicated Lloydminster gas oil contained 47.8 wt.% saturates, 18.1 wt.% monoaromatics, 26.8 wt.%

higher aromatics and polars. A comparison of this feedstock with the IPL Vacuum Gas Oil used previously showed IPL to be a higher API gravity (24.6°), lower sulphur (0.49 wt.%) feed with a high carbon forming tendency (0.78 wt.%) and higher distillation range (333 - 555°C). Compositions and, therefore, fuel precursors also differed, with IPL having a higher percentage of saturates (63.4 wt.%) and monoaromatics (13.7 wt.%), which favoured more gas + gasoline yield with less light cycle oil, decant oil and coke yields.

The following relationships were used to estimate the cracked product precursors shown in Table 3:

gas + gasoline = saturates + monoaromatics
light cycle oil = diaromatics + 2 ring aromatic sulphur + 1/2 (3 ring aromatic sulphur)

decant oil + coke = 100 - light cycle oil - (gas + gasoline)

Effect of Hydrogenation on Physical Properties

The characterization study (Table 1) reveals that as the hydrogen consumption increased, the API gravity and aniline point also increased due to a reduction in aromatic content. Run 15-28 (Condition #3) showed the greatest change in aromatic content from the feed.

The effects of increased hydrogenation on sulphur and nitrogen levels in Lloydminster gas oil are plotted in Figures 1a and 1b. Hydrogen consumption as low as 300 SCFB dramatically reduced sulphur levels with either NT-550 or NM-506 catalyst. Effective removal of nitrogen compounds from the Lloydminster gas oil required much greater hydrogen consumption (>600 SCFB) which was only possible with NM-506 catalyst.

Conradson carbon residue results reflect the coke forming tendency of the gas oil and the data in Table 1 indicates all the hydrogenation conditions significantly reduced this tendency. Run 15-18 (Condition #3) had the lowest Conradson carbon of the hydrogenated feeds.

Metals levels in Lloydminster gas oil were reduced when the feed was hydrogenated.

Compositional changes associated with increased hydrogen consumption are plotted in Figures 2a and 2b. Hydrogenation had the greatest effect on cycloparaffins levels. The paraffins and monoaromatics were not significantly affected by any hydrogenation condition.

NM-506 catalyst produced the greatest increase in cycloparaffins level which in turn yielded the highest level of gas + gasoline precursors (86.7%) as shown in Table 3.

Effects of Hydrogenation on Microactivity Tests (MAT)

All MAT tests were carried out at as close to a C/O ratio of 4 as possible, but since some variation occurred, and since conversion vs. C/O ratio is not a linear relationship, care must be exercised when comparing the MAT data from one run to the next. A comparison of MAT data of the feed versus hydrogenated products is plotted in Figures 3a and 3b. Both NT-550 and NM-506 catalysts effectively reduced coke at reaction condition #3. Maximum conversion and C_5^+ gasoline yield were only possible with reaction condition #3 and NM-506 catalyst. Accurate comparison of MAT data to predict yield improvements with hydrogenation is not recommended since some variation in C/O ratios occurred.

MAT results at two other cat to oil ratios are needed to estimate optimum gasoline yield of each feed and hydrogenated product for accurate comparison and to accurately determine the coke forming propensity of the feed.

Results show condition #3 with NM-506 catalyst will yield feedstock giving maximum conversion and gasoline with minimum coke make.

TABLE 1

Feedstock and Hydrogenated Product Characterization

Lloydminster Gas Oil (D85-8-1)

Hydrogenation Catalyst		NT 550	NT 550	NT 550	NT 550	NM 506	NM 506	NM 506	NM 506
Reaction Condition	Feed	#1	#2	#3	#4	#1	#2	#3	#4
		Run	Run	Run	Run	Run	Run	Run	Run
Characterization		15-8	15-6	15-4	15-7	15-31	15-29	15-28	15-30
+Calculated Hydrogen Consumption SCFB		328	533	538	458	369	480	628	556
% Liquid Volume Yield		100	100	102	95*	99	98	100	87*
Density @ 15°C	0.9238	0.9094	0.9075	0.8987	0.9035	0.9013	0.8986	0.8929	0.8932
API Gravity	21.6	24.0	24.3	25.9	25.0	25.4	25.9	26.9	26.8
Aniline Pt, °C	66.1	73.6	74.0	75.0	73.4	75.0	75.0	78.6	73.8
Conradson Carbon, wt%	0.09	0.019	0.010	0.008	0.008	0.013	0.008	0.004	0.006
Basic Nitrogen, wt%	0.019	0.019	0.016	0.010	0.011	0.015	0.010	0.002	0.002
Total Nitrogen, wt%	0.049	0.048	0.042	0.025	0.033	0.041	0.028	0.005	0.011
Total Sulphur, wt%	2.03	0.44	0.32	0.25	0.17	0.22	0.19	0.10	0.04
cSt @ 40°C	28.89	22.12	21.33	20.69	18.05	20.93	20.47	19.41	14.54
cSt @ 100°C	4.48	3.94	3.87	3 81	3.53	3.83	3.78	3.70	3.12
**VI	34	45	47	49	51	48	48	54	56
Metals µg/g									
Ni	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
V	0.18	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Fe	2.2	0.12	1.10	1.73	0.15	0.25	0.26	0.28	0.23

Note:

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

+ Hydrogen consumptions were determined by a technique called "HYCAL", which calculates the amount of hydrogen consumed in a reaction by comparing mass spec compositional data of the feed and the hydrogenated product.

* Data should be considered suspect due to sampling error in the reactor.

** Viscosity Index (VI) is an arbitrary number used to characterize the variation of the kinematic viscosity of a petroleum product with temperature. For oils of similar kinematic viscosity, the higher the VI the smaller the effect of temperature on its kinematic viscosity.

TABLE 2

Feedstock and Hydrogenated Product Characterization

Lloydminster Gas Oil (D85-8-1)

Hydrogenation Catalyst		NT 550	NT 550	NT 550	NT 550	NM 506	NM 506	NM 506	NM 506
Reaction Condition	Feed	#1	#2	#3	#4	#1	#2	#3	#4
		Run	Run	Run	Run	Run	Run	Run	Run
Characterization		15-8	15-6	15-4	15-7	15-31	15-29	15-28	15-30
G.C.Distillation, °C									
IBP	250	228	219	196	194	240	238	223	206
5%	307	285	280	276	264	287	284	277	257
10%	329	307	303	301	292	306	304	299	282
50%	394	382	380	379	375	379	378	376	365
90%	466	462	461	460	455	453	452	449	439
FBP	552	551	550	548	548	570	583	560	561

Note:

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

TABLE 3

Compositional Analysis of MAT Feeds

Lloydminster Gas Oil (D85-8-1)

Hydrogenation Catalyst		NT 550	NT 550	NT 550	NT 550	NM 506	NM 506	NM 506	NM 506
Reaction Condition	Feed	#1	#2	#3	#4	#1	#2	#3	#4
Run		15-8	15-6	15-4	15-7	15-31	15-29	15-28	15-30
Hydrocarbon Type, wt%									
Paraffins	14.21	14.76	17.34	17.20	16.62	16.78	17.35	16.57	16.59
Monocycloparaffins	11.16	12.68	13.75	13.93	13.26	13.09	14.10	14.89	14.73
Condensed Cycloparaffins	22.39	24.68	27.48	27.99	26.65	26.19	28.30	30.39	28.47
Alkylbenzenes	5.94	10.24	8.90	8.67	9.04	8.58	7.94	8.29	8.43
Benzocycloparaffins	6.11	7.76	7.06	7.73	8.07	7.41	7.05	8.45	9.12
Benzodicycloparaffins	6.08	5.85	5.84	7.19	7.13	5.80	6.53	8.13	8.02
Diaromatics	15.29	13.27	10.72	8.85	10.23	12.07	9.31	7.21	8.23
Triaromatics	5.46	3.89	3.03	2.26	2.58	3.75	2.54	1.36	1.98
Tetraaromatics	2.74	1.41	0.82	0.90	1.08	1.62	1.24	0.72	0.81
Polyaromatics & Polars	3.32	2.19	2.63	2.42	2.62	1.67	2.72	1.41	1.39
Aromatic Sulphur									
2-ring Compounds	3.64	0.92	0.55	0.75	0.80	1.16	0.89	0.81	0.93
3-ring Compounds	2.96	2.09	1.73	1.90	1.71	1.68	1.72	1.57	1.23
4-ring Compounds	0.38	0.11	0.10	0.14	0.12	0.04	0.10	0.13	0.05
Unidentified Hydrocarbons	0.32	0.15	0.05	0.07	0.09	0.16	0.21	0.07	0.02
Total	100.00	100.00	100.00	100.00	100.00	100.0	100.00	100.0	100.00
Precursors									
gas + gasoline	65.89	75.97	80.37	82.71	80.77	77.85	81.27	86.72	85.36
light cycle oil	20.41	15.24	12.13	10.55	11.88	14.07	11.06	8.81	9.78
decant oil + coke	13.70	8.79	7.50	6.74	7.35	8.08	7.67	4.47	4.86

Note:

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

TABLE 4

MAT Product Yield Data

Lloydminster Gas Oil (D85-8-1)

Hydrogenation Catalyst		NT 550	NT 550	NT 550	NT 550	NM 506	NM 506	NM 506	NM 506
Reaction Condition	Feed	#1	#2	#3	#4	#1	#2	#3	#4
Run	LC-31	LC-37	LC-35	LC-34	LC-36	LC-79	LC-68	LC-67	LC-78
Mass Balance, wt%	101.4	102.7	104.2	102.9	96.9	102.9	101.3	101.8	102.3
T, °C	489	490	489	490	490	489	490	490	490
C/O, g/g	4.21	4.27	4.13	3.68	4.55	3.94	4.43	4.00	3.82
Yields, wt% FF									
H_2	0.06	0.08	0.05	0.06	0.08	0.08	0.07	0.07	0.06
CH_4	0.36	0.29	0.21	0.25	0.36	0.27	0.31	0.29	0.28
$<C_2$	2.03	1.07	0.76	0.97	1.23	0.95	1.08	1.08	1.11
ΣC_3	4.92	4.97	4.07	4.58	6.15	4.44	5.15	5.34	5.03
ΣC_4	9.24	9.67	8.42	9.08	12.80	9.23	10.52	10.49	9.74
ΣC_5	4.92	4.63	4.18	4.66	7.17	5.41	5.61	5.27	4.84
C_5^+ gasoline	47.60	52.16	53.00	55.55	52.65	53.04	56.44	60.16	57.64
C_6^+ gasoline	42.68	47.52	48.82	50.89	45.47	47.62	50.82	54.89	52.79
LCO	23.28	21.73	23.25	21.19	19.02	22.05	19.32	17.06	19.91
DO	10.36	8.11	8.60	7.01	6.06	8.16	5.59	4.28	4.97
Coke	2.54	2.27	1.86	1.59	2.06	2.10	1.87	1.56	1.57
Conversion	66.34	70.15	68.13	71.78	74.90	69.77	75.07	78.64	75.10
C_6^+ gasoline/Conversion	0.64	0.68	0.72	0.71	0.61	0.68	0.68	0.70	0.70
Coke/Conversion	0.04	0.03	0.03	0.02	0.03	0.03	0.02	0.02	0.02
C_6^+ gasoline/coke	16.80	20.93	26.20	32.01	22.07	22.68	27.18	35.19	33.62

NOTE: All samples were cracked in the MAT reactor using DA 250 catalyst (MR3-19-1).

DA-250 catalyst (MR3-19-1) - Surface Area (m^2/g) - 73, Pore Volume (cc/g) - 0.23, Bulk Density (g/cc) - 0.97, Nickel (ppm) - 455, Vanadium (ppm) - 1951, Alumina (wt.%) - 35.9, Carbon (wt.%) - 0.23, Particle Size (wt.%) 0 to 20 μ - 2, 0 to 40 μ - 13, 0 to 80 μ - 68, APS μ - 67.

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

FIGURE 1a

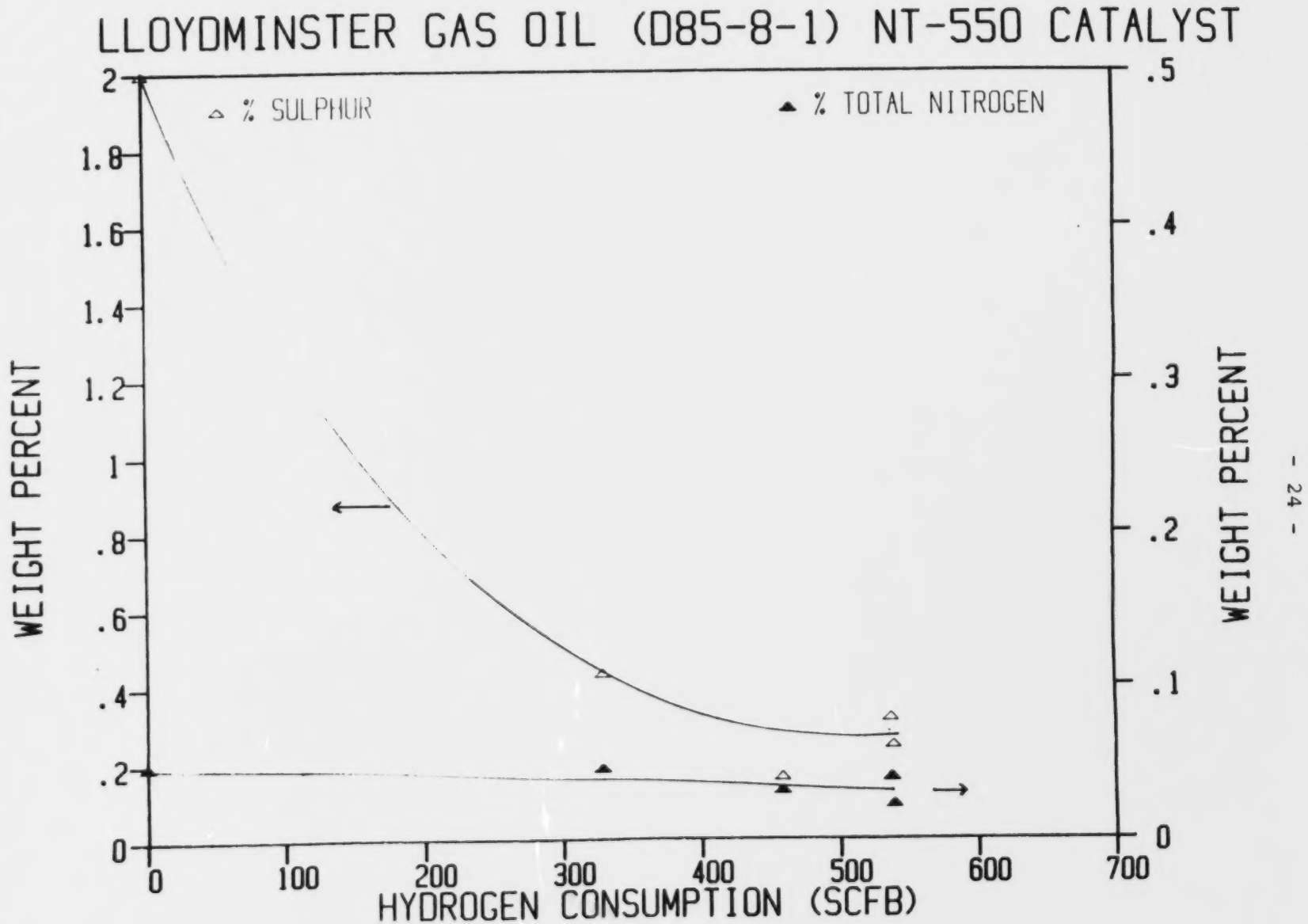

LLOYDMINSTER GAS OIL (D85-8-1) NT-550 CATALYST
△ % SULPHUR
▲ % TOTAL NITROGEN
WEIGHT PERCENT
WEIGHT PERCENT
HYDROGEN CONSUMPTION (SCFB)
0
.2
.4
.6
.8
1
1.2
1.4
1.6
1.8
2
0
.1
.2
.3
.4
.5
0
100
200
300
400
500
600
700

FIGURE 1b

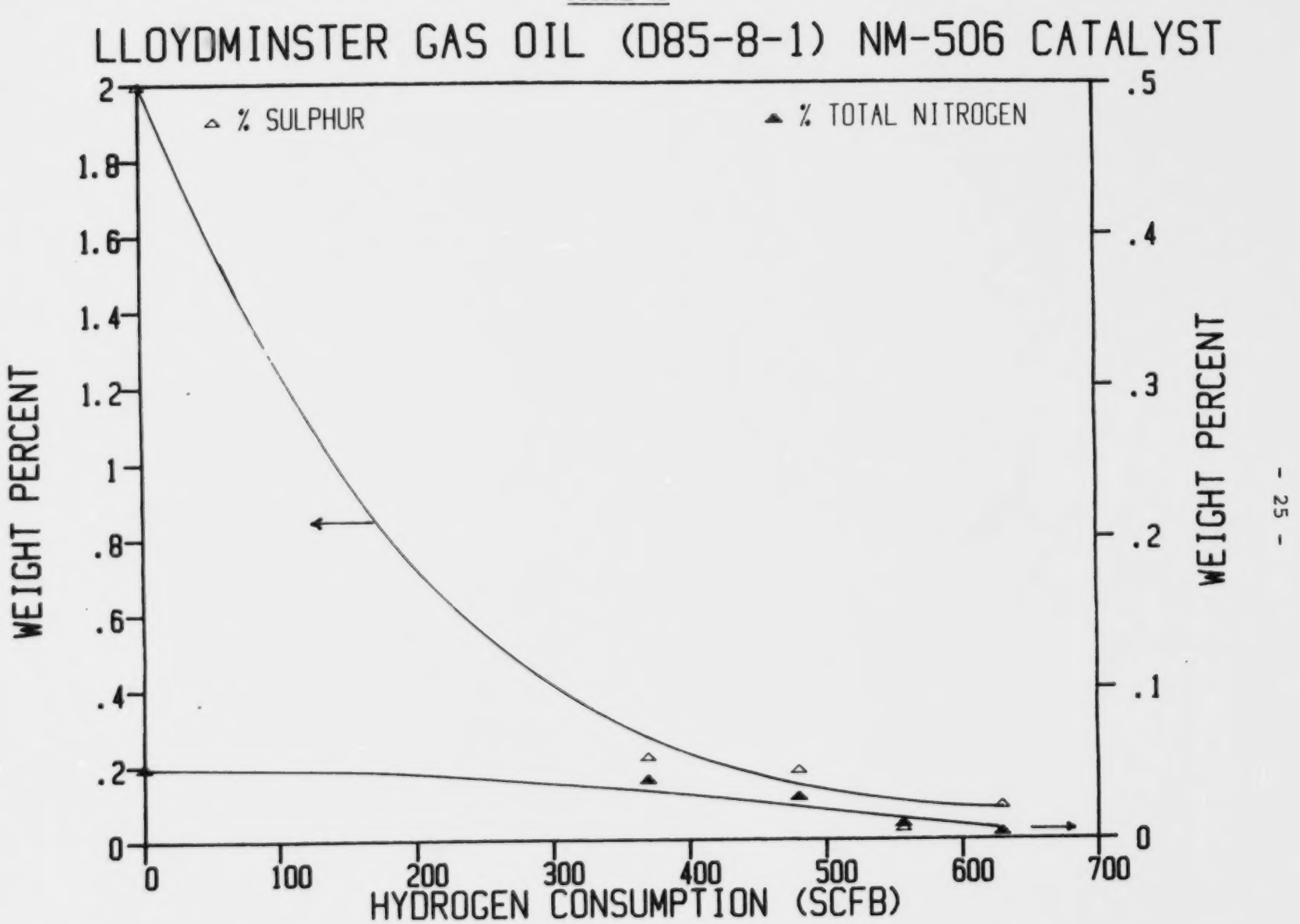

LLOYDMINSTER GAS OIL (D85-8-1) NM-506 CATALYST
△ % SULPHUR
▲ % TOTAL NITROGEN
WEIGHT PERCENT
WEIGHT PERCENT
2
1.8
1.6
1.4
1.2
1
.8
.6
.4
.2
0
.5
.4
.3
.2
.1
0
0
100
200
300
400
500
600
700
HYDROGEN CONSUMPTION (SCFB)

FIGURE 2a

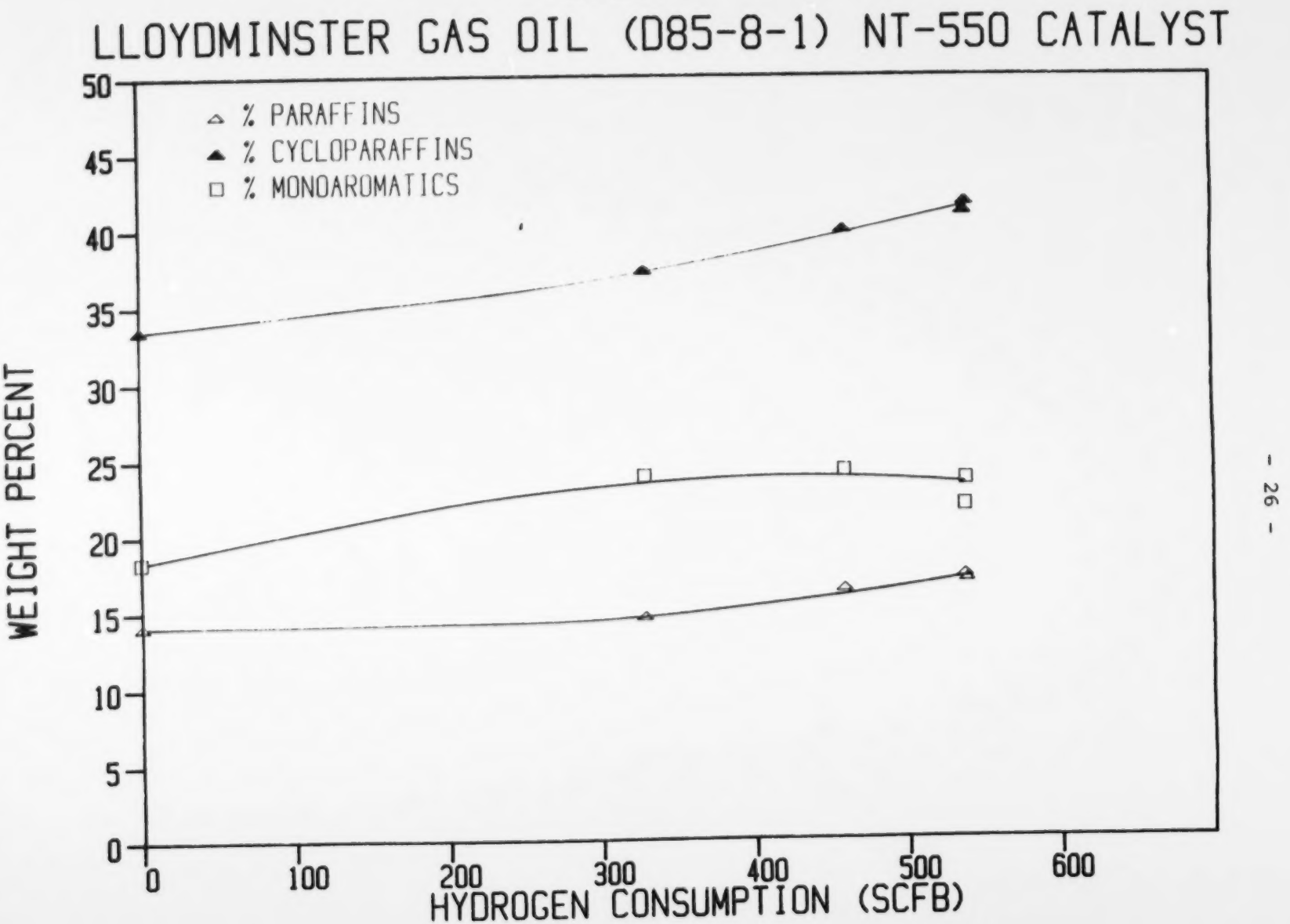

LLOYDMINSTER GAS OIL (D85-8-1) NT-550 CATALYST
% PARAFFINS
% CYCLOPARAFFINS
% MONOAROMATICS
WEIGHT PERCENT
0
5
10
15
20
25
30
35
40
45
50
0
100
200
300
400
500
600
HYDROGEN CONSUMPTION (SCFB)

FIGURE 2b

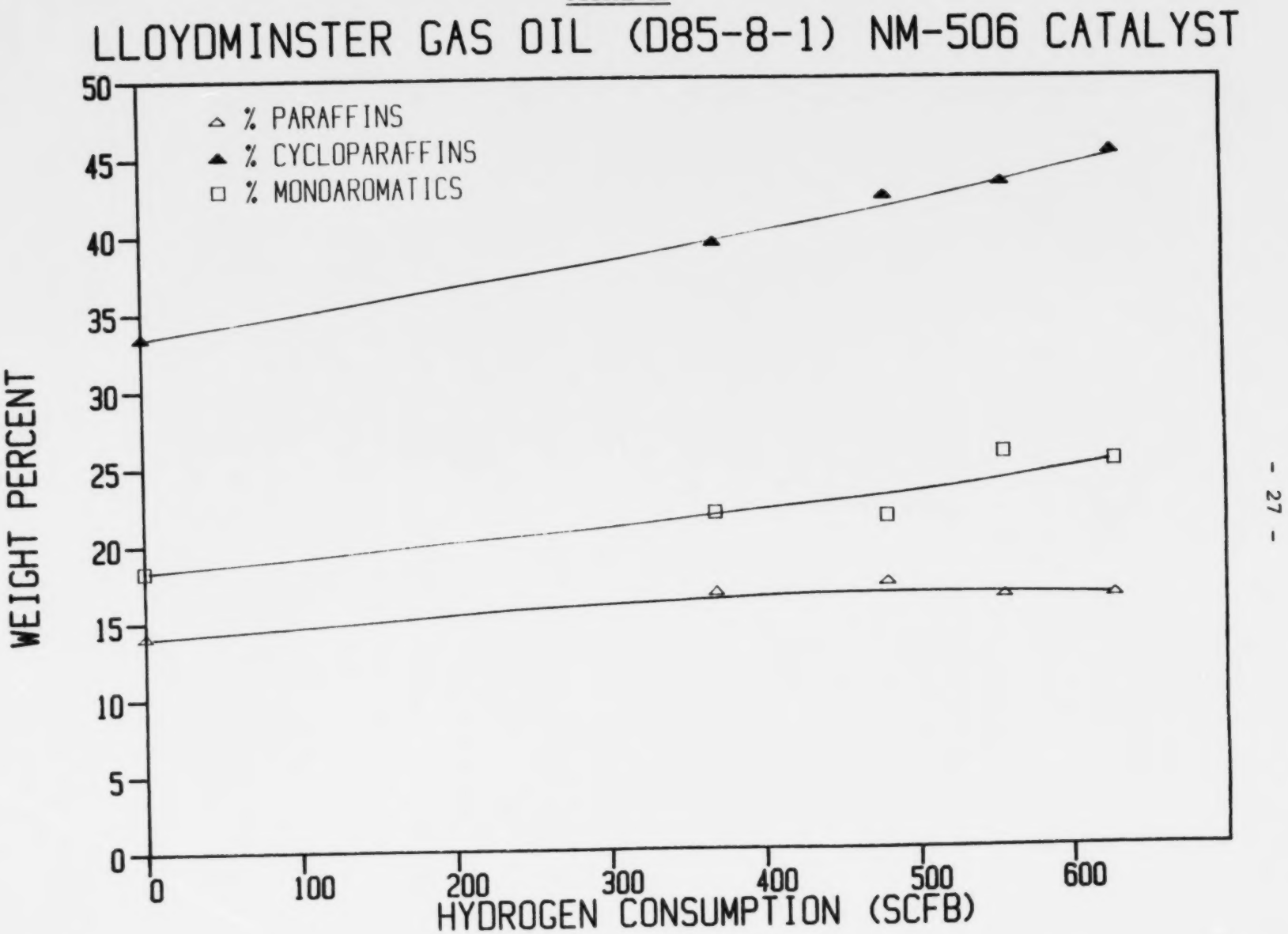

LLOYDMINSTER GAS OIL (D85-8-1) NM-506 CATALYST
% PARAFFINS
% CYCLOPARAFFINS
% MONOAROMATICS
WEIGHT PERCENT
0
5
10
15
20
25
30
35
40
45
50
0
100
200
300
400
500
600
HYDROGEN CONSUMPTION (SCFB)

FIGURE 3a

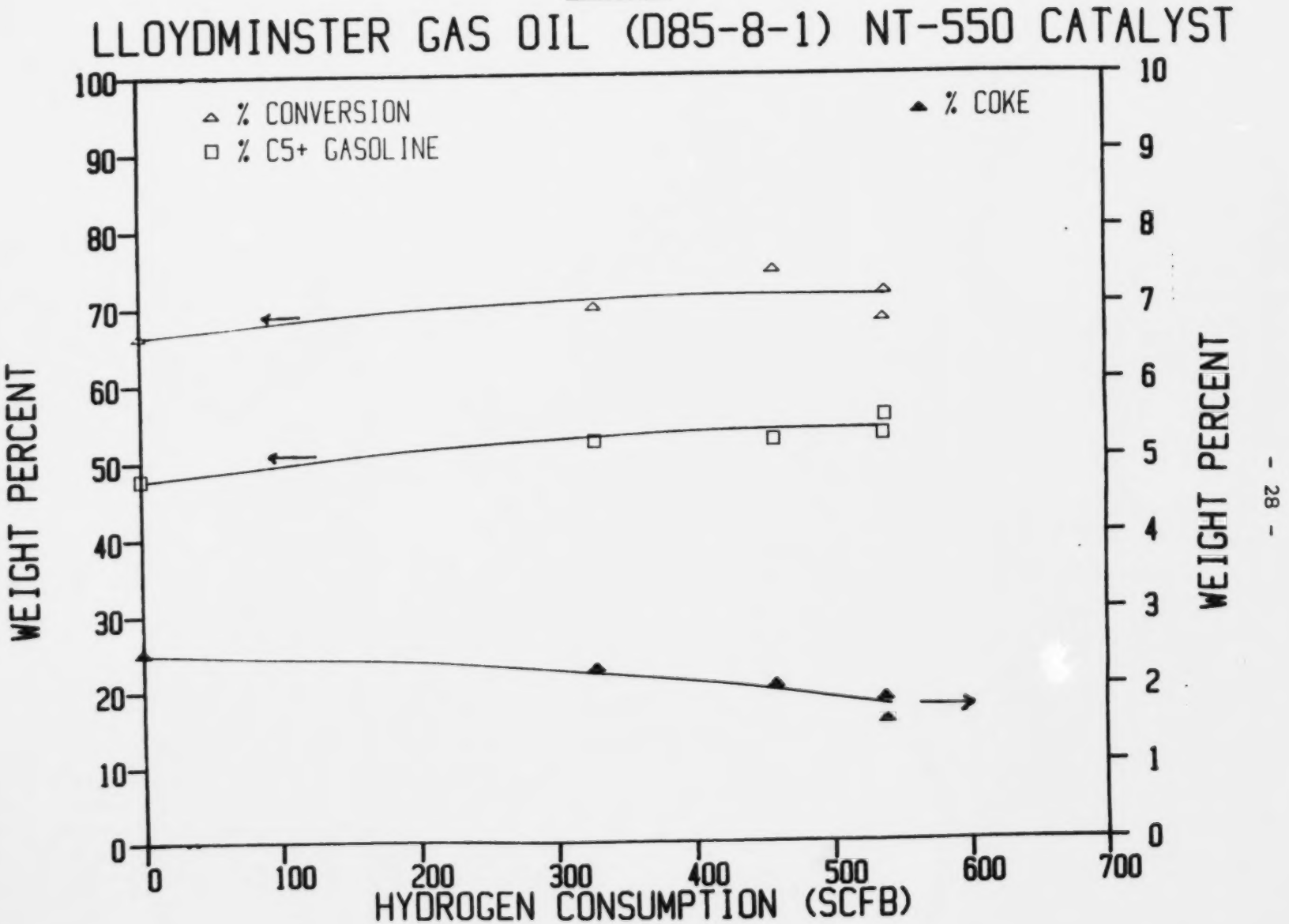
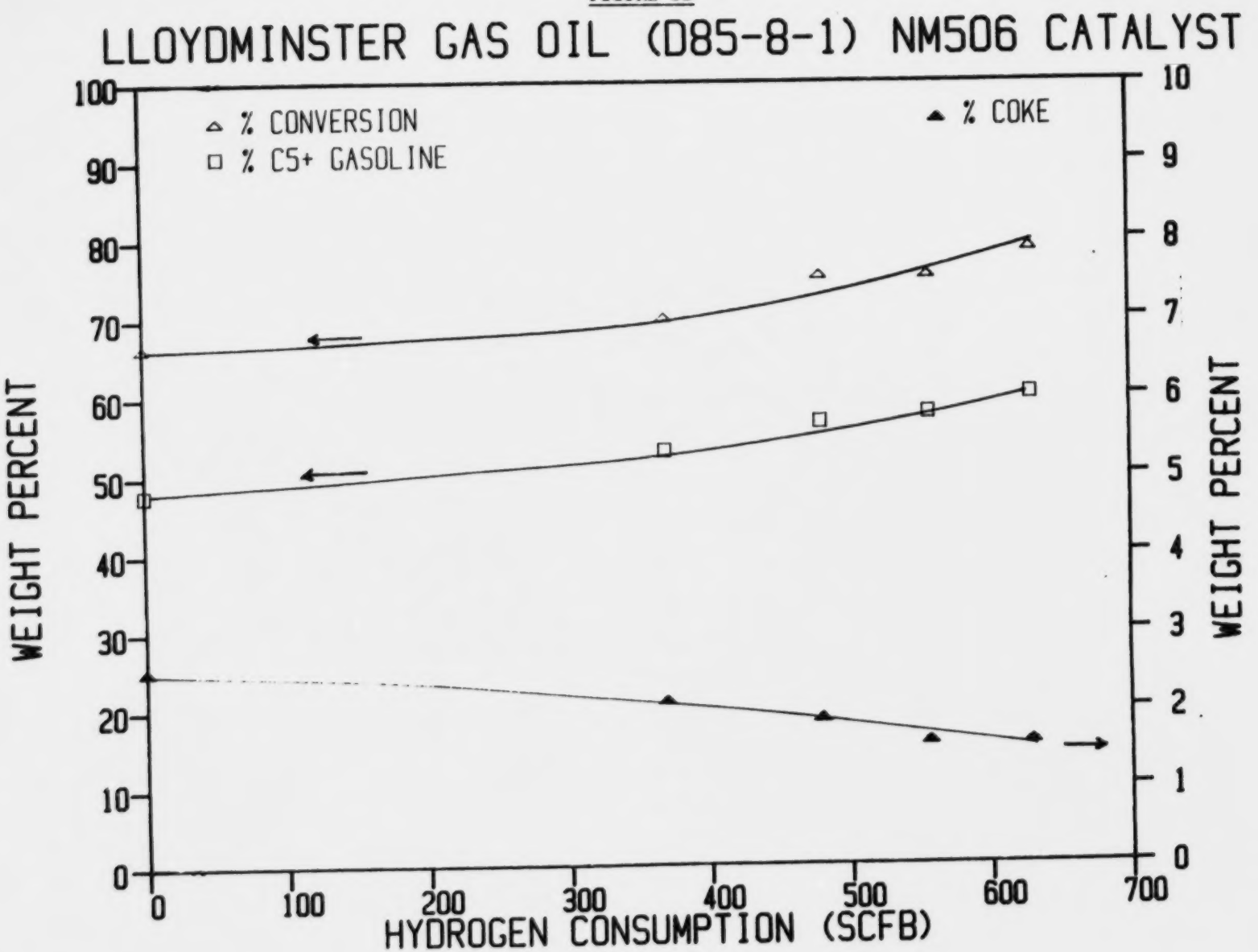

LLOYDMINSTER GAS OIL (D85-8-1) NT-550 CATALYST
% CONVERSION
% C5+ GASOLINE
% COKE
WEIGHT PERCENT
WEIGHT PERCENT
HYDROGEN CONSUMPTION (SCFB)
0
10
20
30
40
50
60
70
80
90
100
0
1
2
3
4
5
6
7
8
9
10
0
100
200
300
400
500
600
700

FIGURE 3b


LLOYDMINSTER GAS OIL (D85-8-1) NM506 CATALYST
△ % CONVERSION
□ % C5+ GASOLINE
▲ % COKE
WEIGHT PERCENT
WEIGHT PERCENT
HYDROGEN CONSUMPTION (SCFB)
0
10
20
30
40
50
60
70
80
90
100
0
1
2
3
4
5
6
7
8
9
10
0
100
200
300
400
500
600
700

2. Rainbow Zama Gas Oil

The Edmonton Rainbow Zama gas oil used in this study was prepared by fractionation of a commercial stream so that its boiling range corresponded to other feedstocks studied (Table 6). This material was a higher API gravity (27.4°) and lower sulphur (0.57 wt.%) feedstock relative to Lloydminster gas oil. Total nitrogen level of the Rainbow Zama gas oil (0.056 wt.%) was similar to that of the Lloydminster gas oil. The higher aniline point (88.5°C) reflects the lower aromatic content of Rainbow Zama gas oil when compared to Lloydminster gas oil.

Coke forming tendency, as measured by Conradson Carbon Residue, was similar to the Lloydminster gas oil (0.12 wt.%).

Compositional data is shown in Table 7 along with the cracking precursor levels. The Rainbow Zama gas oil had a higher percentage of saturates (64.1 wt.%) and less monoaromatics (12.2 wt.%) than Lloydminster gas oil, which favoured more gas and gasoline yield with less light cycle oil yield. Similar decant oil and coke yields were expected with both feeds.

The relationships mentioned previously (p.18) were employed to estimate the cracked product precursors shown in Table 7.

Effects of Hydrogenation on Physical Properties

The physical properties of Rainbow Zama gas oil and its hydrogenated products (Table 5) reveal the same trend with hydrotreating as the Lloydminster gas oil. API gravity and aniline point increased as the hydrogen consumption increased. The effect is the result of a reduction in the aromatic content as hydrogenation took place.

As with Lloydminster gas oil, the reaction condition #3 (343°C, 13.8 MPa, 2 LHSV) with NM-506 catalyst (Run 15-35) showed the greatest reduction in aromatic content.

The effects of increased hydrogenation on sulphur and nitrogen levels in Edmonton gas oil are plotted in Figures 4a and 4b. Reduction of sulphur from 0.57 to 0.1 wt.% required approximately 250 SCFB of hydrogen with either NT-550 or NM-506 catalyst, but as with the Lloydminster gas oil, reduction of nitrogen required much

greater hydrogen consumption (500 SCFB) which was only possible with NM-506. The high pressure operations (13.8 MPa) were also required with both catalysts to remove significant amounts of nitrogen, particularly basic nitrogen.

The carbon forming tendencies of Edmonton Rainbow Zama are reflected in the Conradson carbon residue (Table 5). The data shows any hydrogenation reduced the tendency of the feed to form the carbon residue. This may allow the addition of some resid material to hydrogenated feedstocks and still achieve acceptable coke levels in a catalytic cracker.

Metal poisons (Ni, V) in the Edmonton gas oil were removed during the fractionation of the feed, rather than during hydrogenation. Hydrogenation of Rainbow Zama (Table 6) resulted in the production of lighter boiling materials. Off gases from the P-15 reactor showed reaction condition #1 and #2 had not caused any cracking of the feed. The lower boiling hydrocarbons in these conditions were the result of H_2 substitution reactions. Slight cracking was observed with conditions #3 and #4.

Selected compositional data from Table 7 are plotted in Figures 5a and 5b.

Hydrogenation had very little effect on the levels of paraffins, cycloparaffins and monoaromatics.

Maximum gas and gasoline precursors, with both catalysts (Table 7), occurred with reaction condition #3 (343°C, 13.8 MPa, 2 LHSV). NT-550 may be the more cost-effective catalyst since it used only half the hydrogen that NM-506 used.

Effects of Hydrogenation on Microactivity Tests (MAT)

All MAT tests were carried out at as close to a C/O ratio of 4 as possible, but since some variation occured and since conversion vs C/O ratio is not a linear relationship, care must be exercised when comparing the MAT data from one run to the next. A comparison of MAT data of the feed versus hydrogenated products is plotted in Figures 6a and 6b. Both catalysts produced hydrogenated feedstocks which gave increased conversion and C_5+ gasoline with reduced coke make. NT-550 catalyst was able to achieve these changes using half the hydrogen consumption (250 SCFB) that NM-506 used.

Accurate comparison of the data would require MAT results at two other catalyst to oil ratios, as discussed previously.

TABLE 5

Feedstock and Hydrogenated Product Characterization

Edmonton Rainbow Zama Gas Oil (D84-100-1)

Hydrogenation Catalyst		NT 550	NT 550	NT 550	NT 550	NM 506	NM 506	NM 506	NM 506
Reaction Condition		#1	#2	#3	#4	#1	#2	#3	#4
	Feed	Run	Run	Run	Run	Run	Run	Run	Run
Characterization	(Note)	15-9	15-10	15-12	15-11	15-32	15-33	15-35	15-34
Calculated Hydrogen Consumption SCFB		50	119	234	176	367	334	481	232
% Liquid Volume Yield		99	108*	98	97	100	100	100	97
Density @ 15°C	0.8899	0.8858	0.8843	0.8809	0.8802	0.8838	0.8816	0.8785	0.8758
API Gravity	27.4	28.2	28.4	29.0	29.2	28.5	28.9	29.5	30.0
Aniline Pt, °C	88.5	90.1	90.8	90.4	89.6	89.7	90.4	92.6	88.6
Conradson Carbon, wt%	0.12	0.032	0.032	0.009	0.036	0.035	0.026	0.015	0.022
Basic Nitrogen, wt%	0.015	0.015	0.015	0.009	0.010	0.014	0.010	0.005	0.004
Total Nitrogen, wt%	0.056	0.051	0.042	0.026	0.034	0.039	0.029	0.009	0.016
Total Sulphur, wt%	0.57	0.15	0.10	0.06	0.04	0.12	0.09	0.05	0.02
cSt @ 40°C	10.48	9.84	10.18	9.91	8.75	9.71	9.24	9.71	7.53
cSt @ 100°C	4.51	4.38	4.41	4.40	3.95	4.35	4.23	4.37	3.60
VI	86	102	85	102	89	104	111	107	109
Metals µg/g									
Ni	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
V	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Fe	0.22	0.39	0.17	0.11	0.42	0.19	0.05	0.11	0.24

(Note) Edmonton Rainbow Zama Gas Oil feed required fractionation.

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

* Data should be considered suspect due to sampling error in the reactor.

TABLE 6

Feedstock and Hydrogenated Product Characterization

Edmonton Rainbow Zama Gas Oil (D84-100-1)

Hydrogenation Catalyst Reaction Condition Characterization	As Received	Feed (Note)	NT 550 #1 Run 15-9	NT 550 #2 Run 15-10	NT 550 #3 Run 15-12	NT 550 #4 Run 15-11	NM 506 #1 Run 15-32	NM 506 #2 Run 15-33	NM 506 #3 Run 15-35	NM 506 #4 Run 15-34
G.C.Distillation, °C										
IBP	246	241	224	236	235	208	242	234	242	200
5%	308	291	285	287	285	268	290	280	285	258
10%	336	317	311	311	309	296	313	305	307	287
50%	446	414	410	410	408	401	407	405	404	390
90%	548	493	490	489	489	483	481	480	479	470
FBP	622	566	562	561	561	559	583	578	584	577

(Note) Edmonton Rainbow Zama Gas Oil feed required fractionation.

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

TABLE 7

Compositional Analysis of MAT Feeds

Edmonton Rainbow Zama Gas Oil D84-100-1

Hydrogenation Catalyst Reaction Condition Run	As Received	Feed (Note)	NT 550 #1 15-9	NT 550 #2 15-10	NT 550 #3 15-12	NT 550 #4 15-11	NM 506 #1 15-32	NM 506 #2 15-33	NM 506 #3 15-35	NM 506 #4 15-34
Hydrocarbon Type, wt%										
Paraffins	26.52	27.53	27.11	29.40	30.12	30.76	30.82	31.42	32.25	31.47
Monocycloparaffins	13.93	14.86	14.46	14.73	15.21	14.97	14.45	14.60	15.50	15.43
Condensed Cycloparaffins	23.69	24.97	24.76	25.67	27.20	25.14	23.16	24.47	26.41	25.62
Alkylbenzenes	4.62	4.66	5.35	4.93	4.72	5.12	6.33	6.01	5.23	4.38
Benzocycloparaffins	4.06	3.70	4.65	4.74	4.78	5.16	5.20	5.03	4.94	4.86
Benzodicycloparaffins	3.56	3.36	4.15	4.78	5.54	5.41	4.63	5.16	5.73	3.65
Diaromatics	9.12	8.83	8.38	7.21	5.97	7.00	8.37	7.25	5.89	7.29
Triaromatics	3.91	3.96	3.38	2.80	1.68	2.28	2.93	2.08	1.28	2.97
Tetraaromatics	1.54	1.83	1.19	0.78	0.29	0.20	0.49	0.51	0.01	1.38
Polyaromatics & Polars	5.88	2.78	4.32	2.66	2.41	2.02	2.57	1.80	1.51	1.57
Aromatic Sulphur										
2-ring Compounds	0.98	0.96	0.57	0.49	0.32	0.14	0.17	0.08	0.12	0.58
3-ring Compounds	1.20	1.52	1.05	1.12	1.16	0.69	0.87	0.99	1.07	0.71
4-ring Compounds	0.32	0.37	0.16	0.15	0.19	0.18	0.01	0.17	0.05	0.04
Unidentified Hydrocarbons	0.67	0.67	0.47	0.54	0.41	0.93	0.00	0.43	0.01	0.05
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Precursors										
gas + gasoline	76.38	79.08	80.48	84.25	87.57	86.56	84.59	86.69	90.06	85.41
light cycle oil	10.70	10.55	9.47	8.36	6.87	7.49	8.98	7.83	6.55	8.22
decant oil + coke	12.92	10.37	10.05	7.39	5.56	5.95	6.43	5.48	3.39	6.37

(Note) Edmonton Rainbow Zama Gas Oil feed required fractionation.

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

TABLE 8

MAT Product Yield Data

Edmonton Rainbow Zama Gas Oil D84-100-1

Catalyst			NT 550	NT 550	NT 550	NT 550	NM 506	NM 506	NM 506	NM 506
Reaction Condition	As Received	Feed (Note)	#1	#2	#3	#4	#1	#2	#3	#4
Run	LC-107	LC-30	LC-38	LC-39	LC-99	LC-40	LC-80	LC-81	LC-104	LC-102
Mass Balance, wt%	102.6	101.6	101.7	101.3	102.7	103.4	103.9	103.5	103.6	101.7
T, °C	490	491	490	490	490	491	490	490	490	490
C/O, g/g	3.70	4.09	4.25	4.41	3.76	3.99	4.02	4.13	3.69	3.82
Yields, wt% FF										
H_2	0.08	0.07	0.09	0.09	0.08	0.08	0.10	0.08	0.08	0.07
CH_4	0.35	0.31	0.27	0.32	0.28	0.24	0.30	0.25	0.28	0.30
$<C_2$	1.14	1.09	0.83	1.04	0.92	0.74	0.96	0.82	0.90	0.95
ΣC_3	4.70	4.77	4.87	5.28	5.38	4.67	5.04	4.94	5.58	5.31
ΣC_4	9.18	9.81	10.49	10.51	11.23	10.02	10.44	10.25	11.06	10.23
ΣC_5	5.07	5.55	5.75	5.10	5.94	5.21	5.88	6.22	5.70	4.83
C_5^+ gasoline	53.61	46.33	52.69	51.60	58.60	52.22	54.76	55.92	60.68	59.02
C_6^+ gasoline	48.53	40.77	46.94	46.50	52.65	47.00	48.87	49.69	54.97	54.18
LCO	19.91	23.71	20.34	21.39	17.31	22.51	19.37	19.20	16.27	17.83
DO	8.22	12.00	8.57	7.92	4.65	8.01	7.39	6.64	3.66	4.68
Coke	3.21	2.26	2.17	2.21	1.88	1.80	2.02	2.20	1.82	1.96
Conversion	71.86	64.27	71.08	70.68	78.03	69.47	73.23	74.14	80.05	77.48
C_6^+ gasoline/Conversion	0.67	0.63	0.66	0.66	0.67	0.68	0.67	0.67	0.69	0.70
Coke/Conversion	0.04	0.04	0.03	0.03	0.02	0.03	0.03	0.30	0.02	0.02
C_6^+ gasoline/coke	15.11	18.04	21.63	21.04	28.01	26.11	24.20	22.59	30.20	27.64

(Note) All samples were cracked in the MAT reactor using DA 250 catalyst (MR3-19-1) and the hydrogenated products were obtained using fractionated Edmonton Rainbow Zama Gas Oil.

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

FIGURE 4a

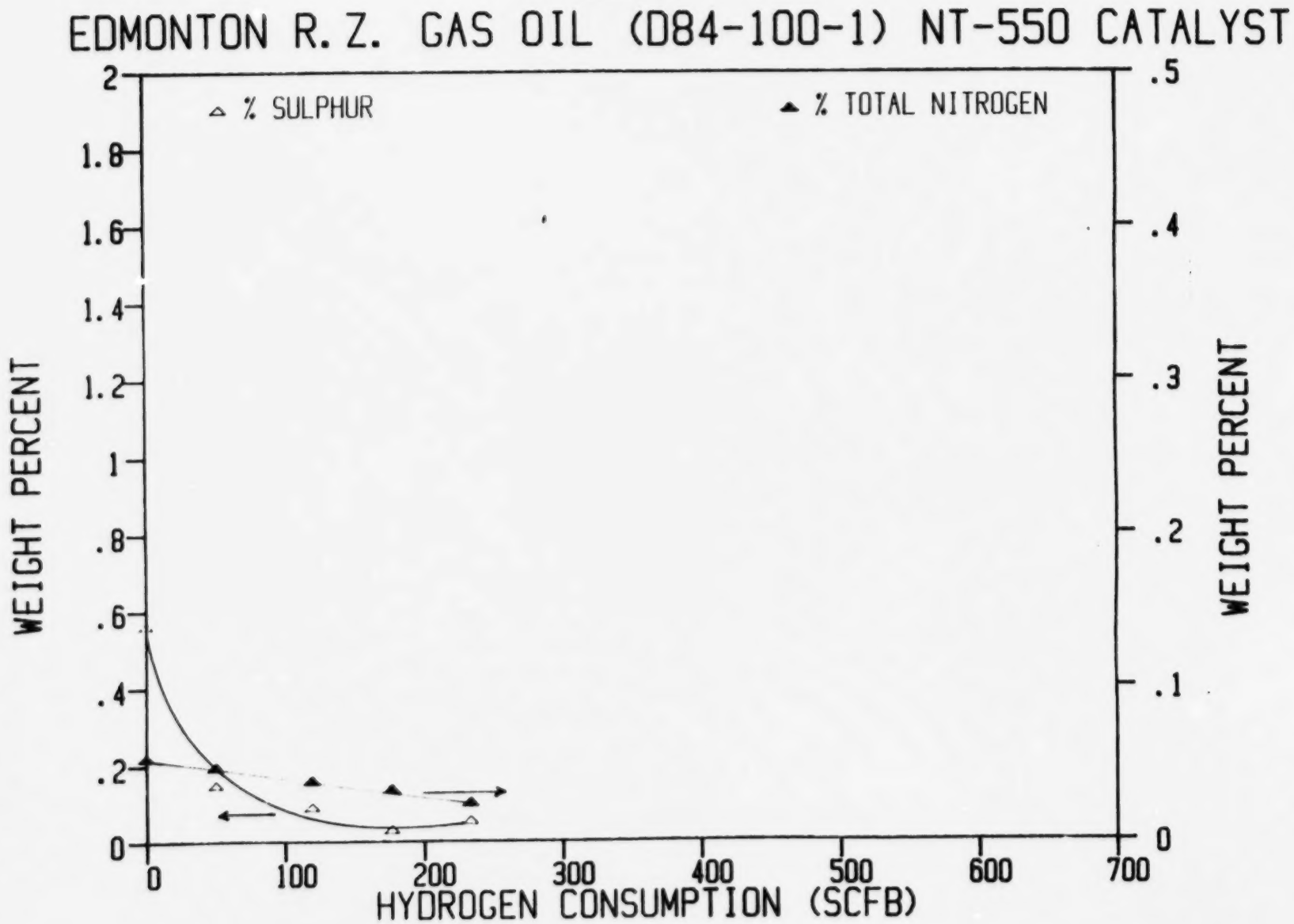

EDMONTON R. Z. GAS OIL (D84-100-1) NT-550 CATALYST
△ % SULPHUR
▲ % TOTAL NITROGEN
WEIGHT PERCENT
WEIGHT PERCENT
HYDROGEN CONSUMPTION (SCFB)
0
.2
.4
.6
.8
1
1.2
1.4
1.6
1.8
2
0
.1
.2
.3
.4
.5
0
100
200
300
400
500
600
700

FIGURE 4b

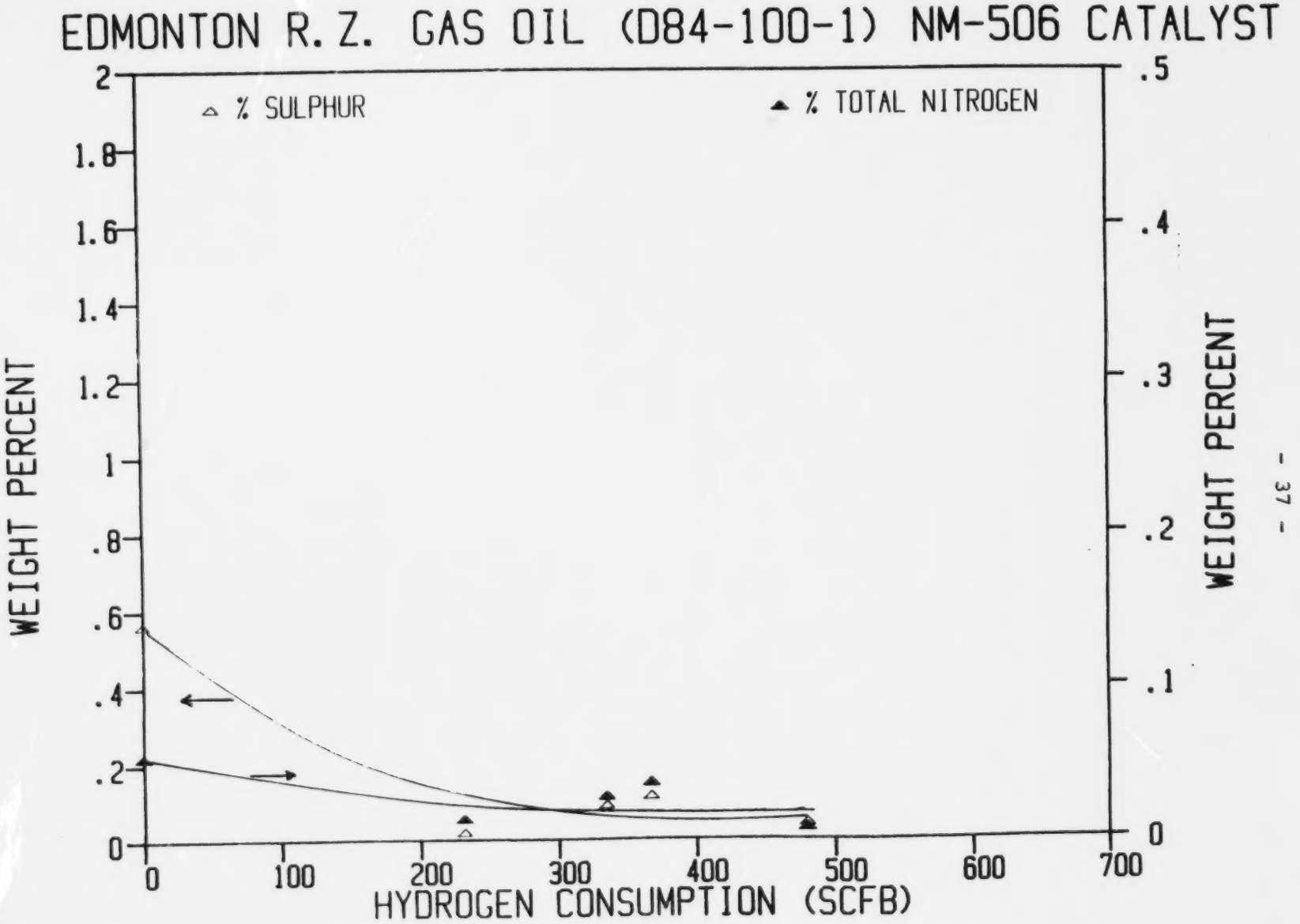

EDMONTON R. Z. GAS OIL (D84-100-1) NM-506 CATALYST
△ % SULPHUR
▲ % TOTAL NITROGEN
WEIGHT PERCENT
WEIGHT PERCENT
2
1.8
1.6
1.4
1.2
1
.8
.6
.4
.2
0
.5
.4
.3
.2
.1
0
0
100
200
300
400
500
600
700
HYDROGEN CONSUMPTION (SCFB)

FIGURE 5a

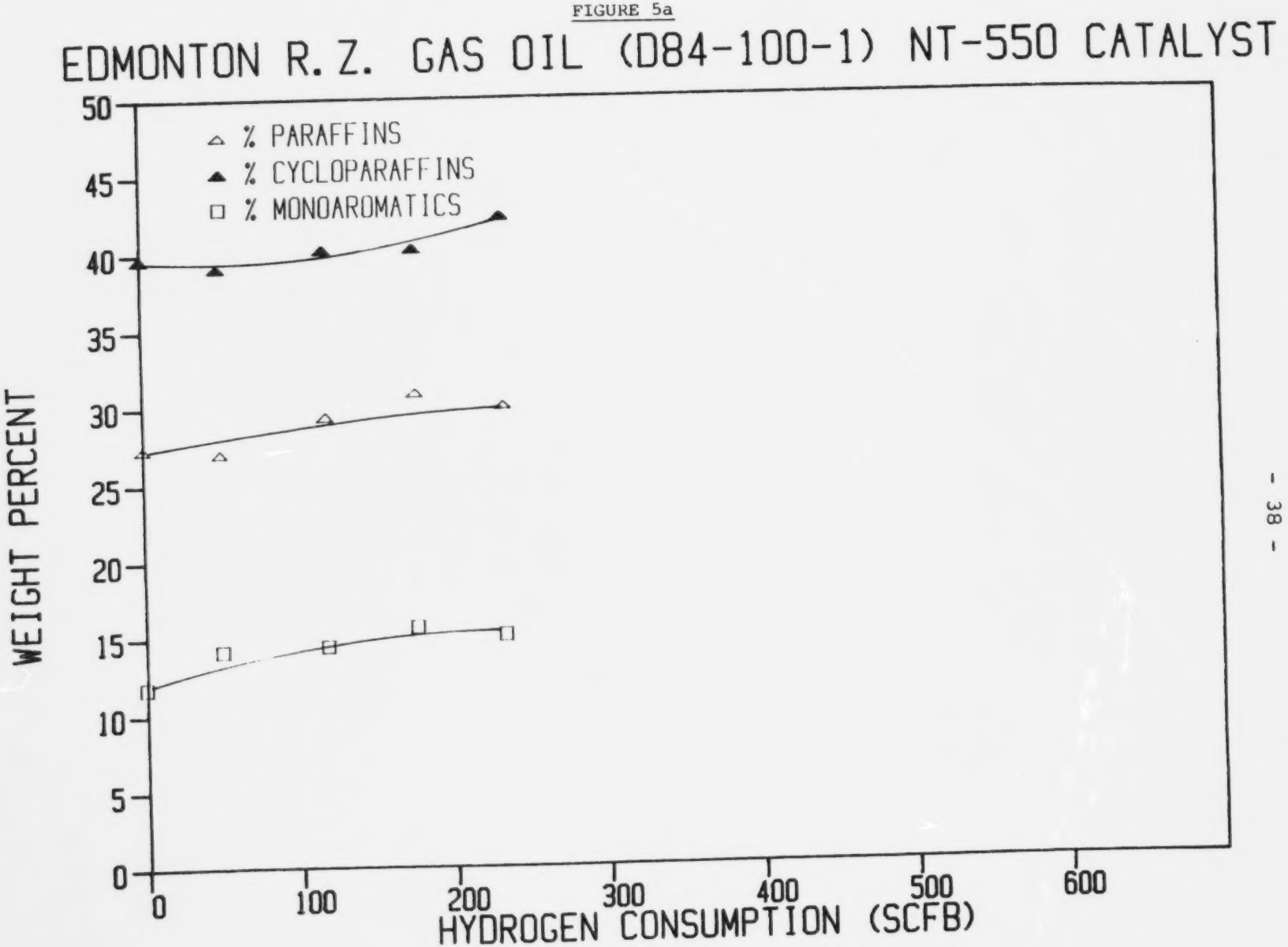

EDMONTON R. Z. GAS OIL (D84-100-1) NT-550 CATALYST
% PARAFFINS
% CYCLOPARAFFINS
% MONOAROMATICS
WEIGHT PERCENT
0
5
10
15
20
25
30
35
40
45
50
0
100
200
300
400
500
600
HYDROGEN CONSUMPTION (SCFB)

FIGURE 5b

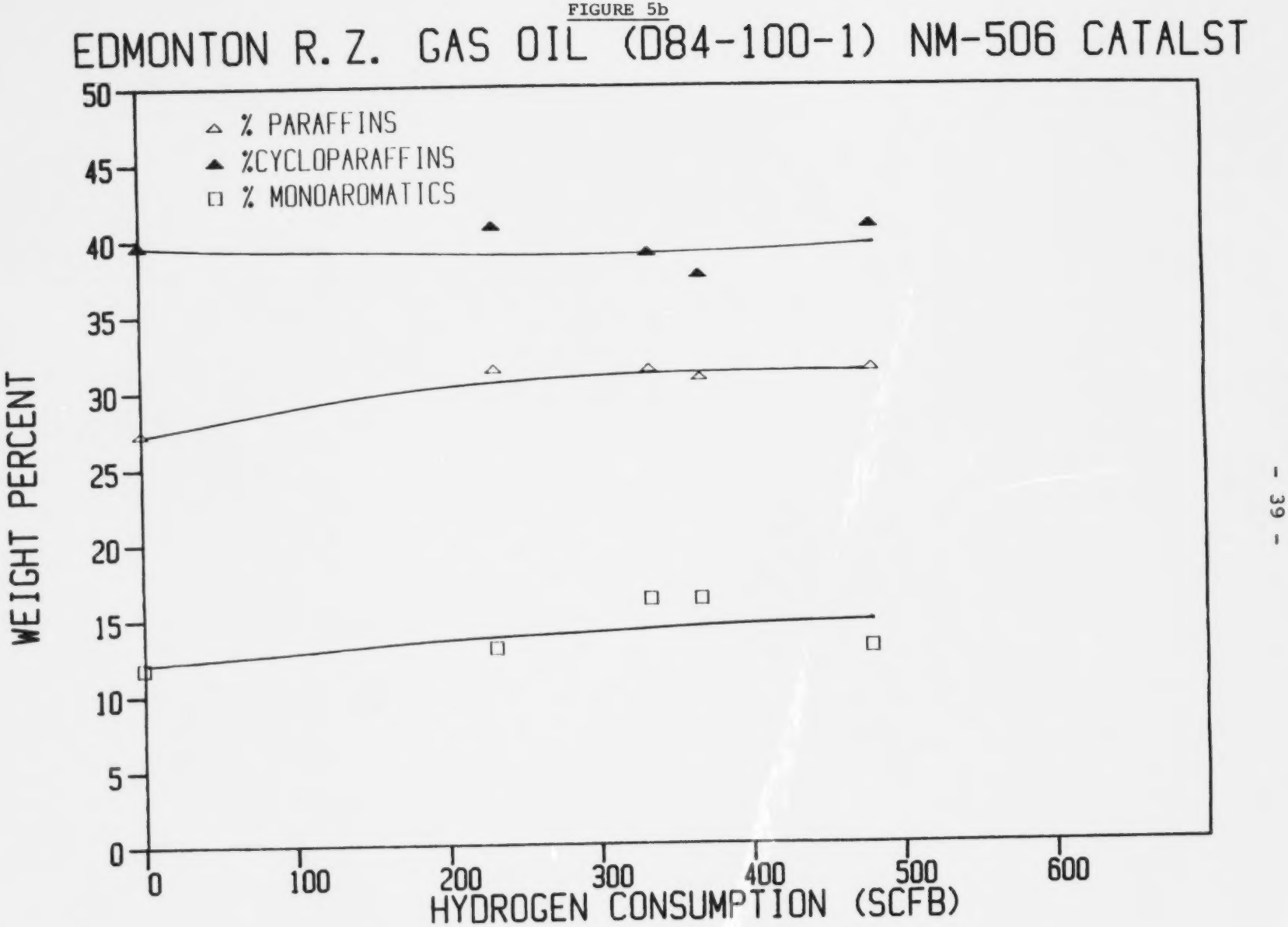

EDMONTON R. Z. GAS OIL (D84-100-1) NM-506 CATALST
% PARAFFINS
%CYCLOPARAFFINS
% MONOAROMATICS
WEIGHT PERCENT
HYDROGEN CONSUMPTION (SCFB)
0
5
10
15
20
25
30
35
40
45
50
0
100
200
300
400
500
600

FIGURE 6a

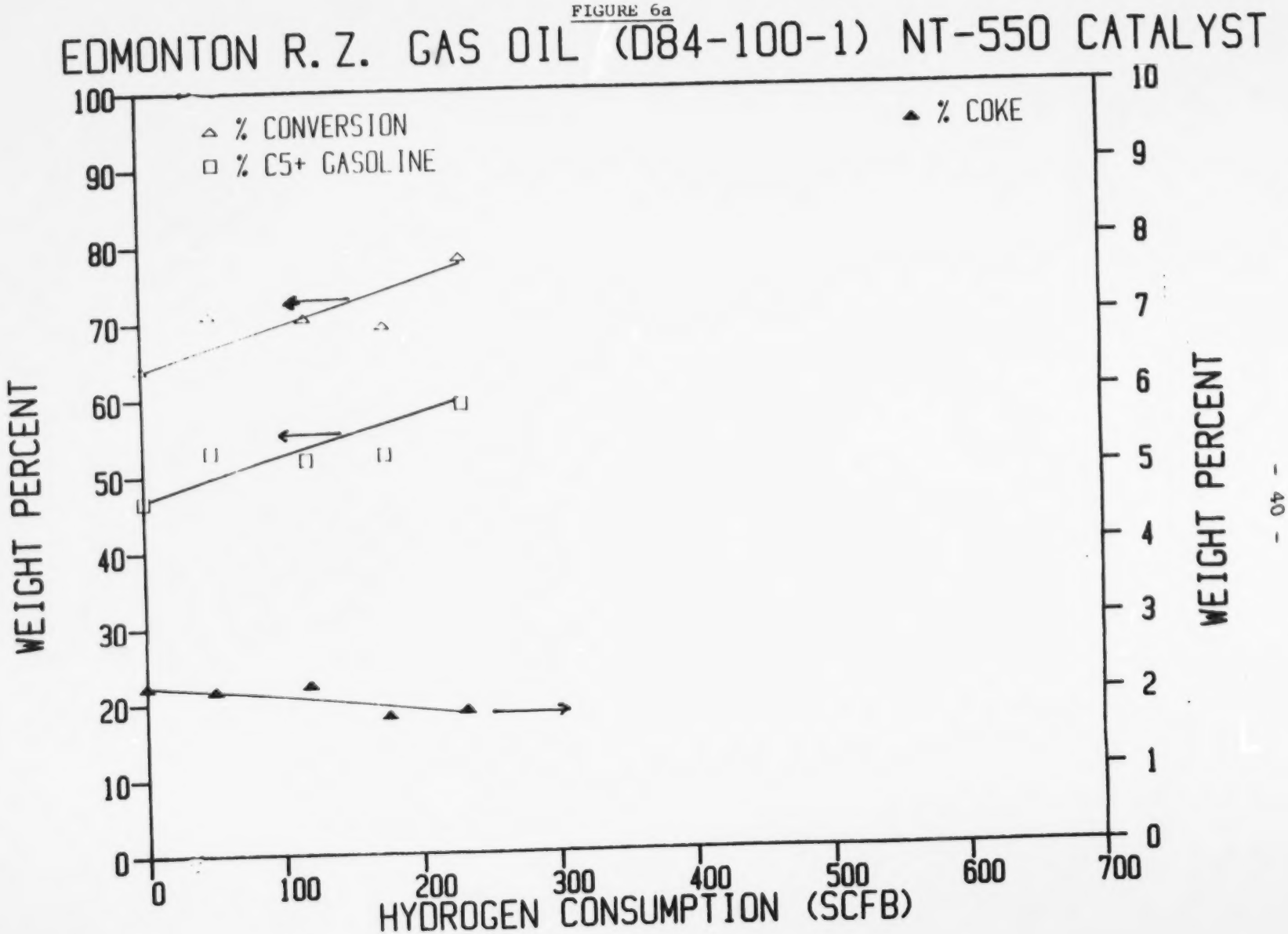
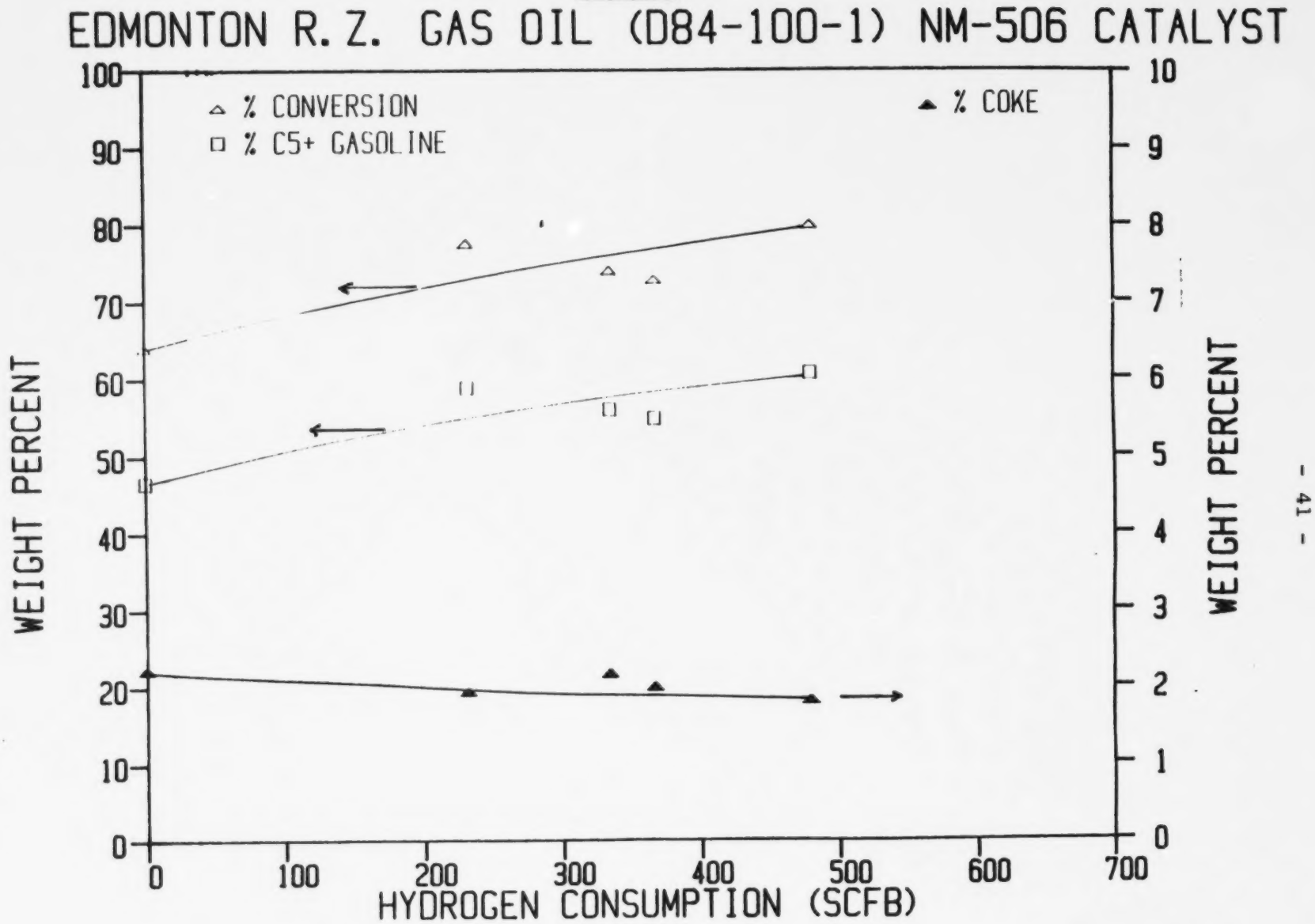

EDMONTON R. Z. GAS OIL (D84-100-1) NT-550 CATALYST
% CONVERSION
% C5+ GASOLINE
% COKE
WEIGHT PERCENT
WEIGHT PERCENT
HYDROGEN CONSUMPTION (SCFB)
0
10
20
30
40
50
60
70
80
90
100
0
1
2
3
4
5
6
7
8
9
10
0
100
200
300
400
500
600
700

FIGURE 6b


EDMONTON R. Z. GAS OIL (D84-100-1) NM-506 CATALYST
% CONVERSION
% C5+ GASOLINE
% COKE
WEIGHT PERCENT
WEIGHT PERCENT
HYDROGEN CONSUMPTION (SCFB)
0
10
20
30
40
50
60
70
80
90
100
0
1
2
3
4
5
6
7
8
9
10
0
100
200
300
400
500
600
700

3. Syncrude Gas Oil

Feed Evaluation

Physical characteristics of Syncrude gas oil (Table 9) show that it was a lower API gravity gas oil (20.2°) with less sulphur (0.24 wt.%) than either the Lloydminster or Rainbow Zama gas oils. The total nitrogen level of the Syncrude gas oil (0.089 wt.%), however, was higher than that for either of these two gas oils. Aniline point of the Syncrude (56.5°C) was lower than the Lloydminster and Rainbow Zama gas oils indicating a higher aromatic content, which is consistent with its processing.

Coke forming tendency, as measured by Conradson carbon residue, was similar to the Lloydminster and Rainbow Zama gas oils (0.09 wt.%).

The boiling range shown in Table 10 had a 260°C 5% point with a 469°C 90% boiling point. This was similar to the other gas oils in the study.

The compositional data and fuel precursors levels are given in Table 11 and show Syncrude was a less saturated gas oil (43.1 wt.% saturation) with more monoaromatics (27.0 wt.%) than either the Lloydminster or Rainbow Zama feeds. The fuel precursors in Table 11 were similar to the Lloydminster gas oil, which favoured less gas + gasoline yield, more light cycle oil yield and similar coke and decant oil to the Rainbow Zama gas oil.

Effect of Hydrogenation on Physical Properties

The characterization study (Table 9) reveals the same trend as the Lloydminster and Rainbow Zama gas oil with API gravity and aniline point increasing as hydrogen consumption and saturation are increased. These changes were the result of a lowering of aromatics content with hydrogenation. Unlike the previous gas oils, both catalysts were equally effective at reducing the aromatics content with reaction condition #3 (343°C, 13.8 MPa, 2 LHSV).

The effect of hydrogen consumption on sulphur and nitrogen levels for hydrotreated Syncrude gas oil is plotted in Figures 7a and 7b.

Increased hydrogen consumption did not significantly reduce sulphur or nitrogen levels in Syncrude gas oil.

Conradson carbon residue results (Table 9) of the Syncrude gas oil were not as affected by hydrogenation as the previous gas oils. Since the processing of Syncrude involves a hydrotreating step, it was expected that the carbon forming tendencies, sulphur levels and nitrogen levels could not be improved to the same extent as conventional gas oils with hydrogenation.

The Syncrude feed, like the Rainbow Zama feed, contained no metal poisons (Ni, V).

GC analyses in Table 10 show very little change in distillation with increased hydrogenation. Since Syncrude has already been hydrotreated, most of the easily hydrogenated sights have been saturated and only condition #4 produced some lighter boiling material.

Selected compositional data from Table 11 are plotted in Figures 8a and 8b. Hydrogenation with NT-550 caused some increase in the monoaromatics level, while NM-506 affected only the cycloparaffins level. Table 11 compositional data was used to estimate the amount of catalytic cracking precursors. Condition #3 with NM-506 gave the maximum amount of gas + gasoline precursors at 80.3 wt.%. However, the hydrogenation of Syncrude did not give as great an improvement in gas + gasoline precursors as the previous conventional gas oils.

Effects of Hydrogenation on Microactivity Tests (MAT)

All MAT tests were carried out at approximately standard conditions (493°C, C/O 4); however, some variation occurred and conversion is only quite relative. The comparison of selected MAT data versus hydrogen consumption is plotted in Figures 9a and 9b. Increased hydrogen consumption did not significantly change the conversion, gasoline production or coke make of Syncrude gas oil. Runs with NM-506 catalyst showed slight improvement in the Syncrude gas was possible, but processing cost could outweigh any improvements in conversion, gasoline yield and coke reduction. The only marginal increases in conversion and gasoline may be due to the gasoline precursor levels being increased by naphthenes and benzocycloparaffins. These species may not be readily cracked to gasoline species but may dehydrogenate and revert to LCO species.

TABLE 9

Feedstock and Hydrogenated Product Characterization

Syncrude Gas Oil D84-102-1

Hydrogenation Catalyst		NT 550	NT 550	NT 550	NT 550	NM 506	NM 506	NM 506	NM 506
Reaction Condition	Feed	#1	#2	#3	#4	#1	#2	#3	#4
		Run	Run	Run	Run	Run	Run	Run	Run
Characterization		15-14	15-15	15-17	15-16	15-36	15-37	15-39	15-38
Calculated Hydrogen Consumption SCFB		5	399*	157	158	148	396*	226	245
% Liquid Volume Yield		102	103	98	96	99	99	100	99
Density @ 15°C	0.9320	0.9326	0.9301	0.9213	0.9272	0.9286	0.9260	0.9202	0.9215
API Gravity	20.2	20.1	20.6	22.0	21.0	20.8	21.2	22.2	22.0
Aniline Pt, °C	56.5	56.8	59.2	62.1	57.7	57.0	58.4	62.0	56.0
Conradson Carbon, wt%	0.09	0.076	0.048	0.024	0.030	0.097	0.057	0.028	0.031
Basic Nitrogen, wt%	0.020	0.018	0.017	0.015	0.015	0.042	0.017	0.012	0.012
Total Nitrogen, wt%	0.089	0.086	0.087	0.054	0.080	0.102	0.073	0.047	0.056
Total Sulphur, wt%	0.24	0.15	0.12	0.07	0.07	0.17	0.14	0.10	0.07
cSt @ 40°C	27.13	26.89	27.42	25.92	21.19	25.54	26.80	25.23	17.87
cSt @ 100°C	4.15	4.14	4.18	4.07	3.66	4.02	4.12	4.01	3.32
VI	-4	1	2	3	9	0	-1	3	13
Metals µg/g									
Ni	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	(0.05
V	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	(0.05
Fe	0.7	0.20	0.17	0.29	0.23	0.31	1.2	0.35	0.49

Note:

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

* Results suspect due to light ends loss in preparation of sample for mass spec compositional analysis.

TABLE 10

Feedstock and Hydrogenated Product Characterization

Syncrude Gas Oil D84-102-1

Hydrogenation Catalyst / Reaction Condition / Characterization	Feed	NT 550 #1 Run 15-14	NT 550 #2 Run 15-15	NT 550 #3 Run 15-17	NT 550 #4 Run 15-16	NM 506 #1 Run 15-36	NM 506 #2 Run 15-37	NM 506 #3 Run 15-39	NM 506 #4 Run 15-38
G.C.Distillation, °C									
IBP	196	200	207	196	174	200	214	214	187
5%	260	257	259	254	242	258	261	259	240
10%	287	284	285	280	272	284	285	281	265
50%	376	376	375	371	368	372	370	366	361
90%	469	471	470	468	463	461	459	459	448
FBP	568	561	561	560	552	570	570	566	560

Note:

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

TABLE 11

Compositional Analysis of MAT Feeds

Syncrude Gas Oil D84-102-1

Hydrogenation Catalyst		NT 550	NT 550	NT 550	NT 550	NM 506	NM 506	NM 506	NM 506
Reaction Condition	Feed	#1	#2	#3	#4	#1	#2	#3	#4
Run		15-14	15-15	15-17	15-16	15-36	15-37	15-39	15-38
Hydrocarbon Type, wt%									
Paraffins	6.95	7.03	6.30	6.95	6.78	7.13	6.31	8.45	7.18
Monocycloparaffins	9.17	9.67	10.42	11.06	9.64	10.60	12.14	10.16	11.82
Condensed Cycloparaffins	26.94	27.52	26.59	30.42	27.29	27.94	28.51	32.56	28.71
Alkylbenzenes	8.54	8.14	9.51	8.37	8.93	8.43	9.44	8.20	8.68
Benzocycloparaffins	9.95	9.13	11.05	11.85	11.37	10.17	9.99	9.95	10.61
Benzodicycloparaffins	8.49	8.19	10.78	11.90	11.30	10.54	9.41	10.97	9.42
Diaromatics	16.02	15.19	14.84	10.75	13.82	13.64	13.36	11.20	12.88
Triaromatics	5.51	5.27	4.41	2.38	3.88	4.56	4.64	2.49	4.20
Tetraaromatics	2.10	2.25	0.76	0.76	0.63	1.12	1.37	0.66	1.71
Polyaromatics & Polars	2.74	4.52	2.58	1.74	3.27	2.95	2.10	2.55	1.94
Aromatic Sulphur									
2-ring Compounds	1.27	1.25	0.86	1.26	0.80	0.83	0.78	0.64	0.99
3-ring Compounds	2.06	1.58	1.79	2.11	1.58	1.72	1.68	1.95	1.56
4-ring Compounds	0.13	0.15	0.06	0.32	0.11	0.29	0.27	0.17	0.27
Unidentified Hydrocarbons	0.13	0.11	0.05	0.13	0.60	0.08	0.00	0.05	0.03
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Precursors									
gas + gasoline	70.04	69.68	74.65	80.55	75.31	74.81	75.80	80.29	76.42
light cycle oil	18.32	17.23	16.60	13.06	15.41	15.33	14.98	12.82	14.65
decant oil + coke	11.64	13.09	8.75	6.39	9.28	9.86	9.22	6.89	8.93

Note:

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

TABLE 12

Compositional Analysis of MAT Feeds

Syncrude Gas Oil D84-102-1

Hydrogenation Catalyst		NT 550	NT 550	NT 550	NT 550	NM 506	NM 506	NM 506	NM 506
Reaction Condition	Feed	#1	#2	#3	#4	#1	#2	#3	#4
Run	LC-33	LC-100	LC-43	LC-45	LC-44	LC-105	LC-85	LC-106	LC-86
Mass Balance, wt%	100.4	102.1	102.0	101.1	100.1	104.42	100.1	102.75	101.9
T, °C	490	490	491	490	490	490	489	489	490
C/O, g/g	3.9	3.47	3.93	3.68	3.81	3.77	4.25	3.49	3.74
Yields, wt% FF									
H_2	0.11	0.12	0.11	0.09	0.00	0.10	0.14	0.08	0.10
CH_4	0.28	0.26	0.30	0.26	0.30	0.25	0.33	0.23	0.27
$<C_2$	1.08	1.00	1.11	0.98	0.97	0.94	1.21	0.92	1.02
C_3	4.03	3.84	4.23	4.36	4.49	3.73	4.65	4.03	4.13
C_4	7.82	6.85	7.96	8.25	8.74	6.59	8.77	7.50	7.89
C_5	4.47	3.22	3.87	3.73	4.45	3.51	5.29	3.69	4.43
C_5^+ gasoline	45.58	47.15	45.48	52.85	47.51	48.19	48.67	54.46	50.04
C_6^+ gasoline	41.11	43.92	41.60	49.12	43.06	44.68	43.37	50.76	45.60
LCO	26.75	28.53	28.72	24.46	26.89	27.76	24.66	24.87	25.91
DO	12.38	10.68	10.21	7.37	9.22	10.37	9.44	6.48	9.22
Coke	2.31	1.92	2.25	1.70	2.14	2.39	2.56	1.71	1.76
Conversion	60.85	60.77	61.05	68.16	63.87	61.86	65.89	68.64	64.86
C_6^+ gasoline/Conversion	0.68	0.72	0.68	0.72	0.67	0.72	0.66	0.74	0.70
Coke/Conversion	0.04	0.03	0.04	0.02	0.03	0.04	0.04	0.03	0.03
C_6^+ gasoline/coke	17.80	22.87	18.49	28.90	20.12	18.69	16.94	29.68	25.91

NOTE: All samples were cracked in the MAT reactor using DA 250 catalyst (MR3-19-1).

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

FIGURE 7a

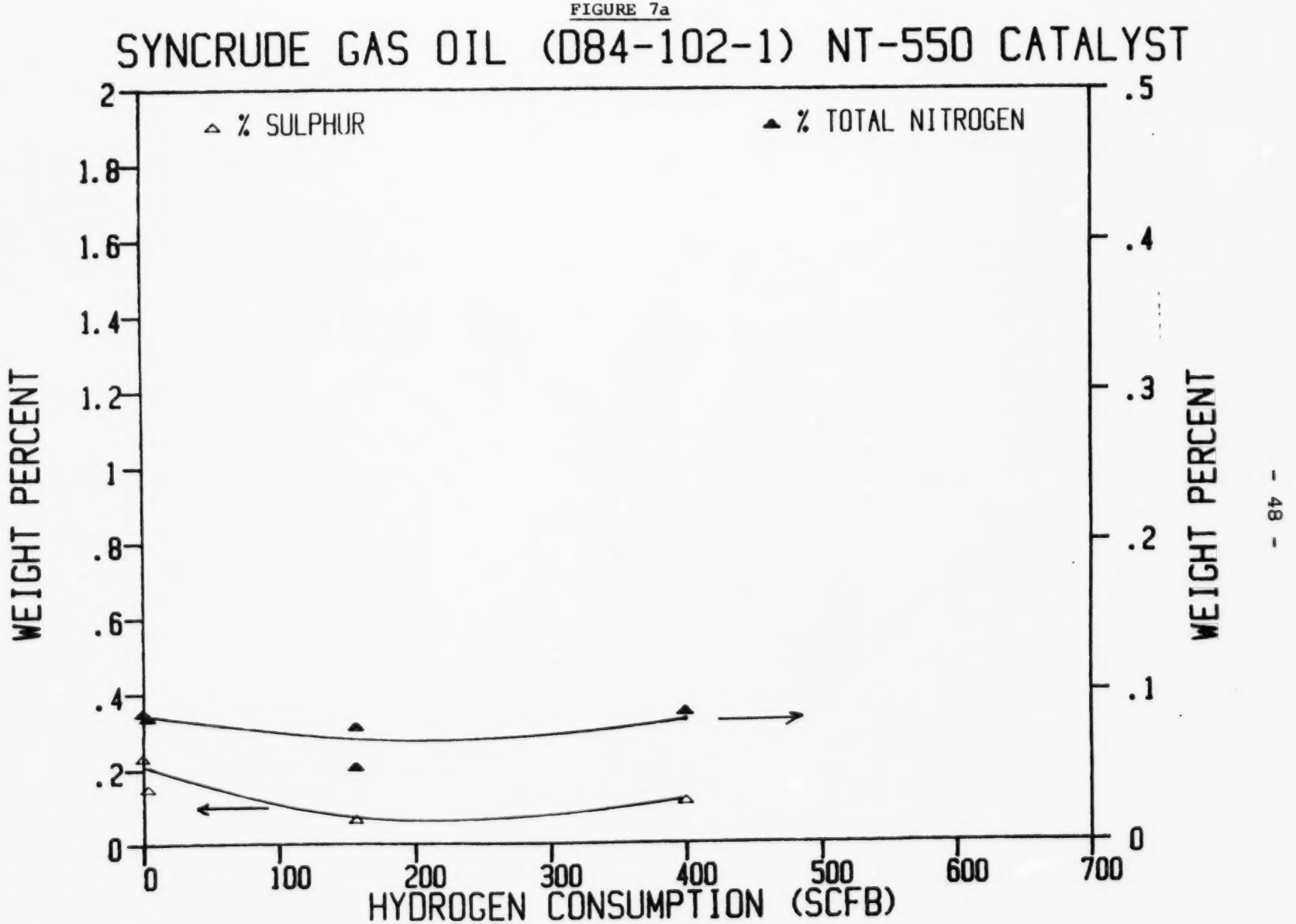

SYNCRUDE GAS OIL (D84-102-1) NT-550 CATALYST
△ % SULPHUR
▲ % TOTAL NITROGEN
WEIGHT PERCENT
WEIGHT PERCENT
2
1.8
1.6
1.4
1.2
1
.8
.6
.4
.2
0
.5
.4
.3
.2
.1
0
0
100
200
300
400
500
600
700
HYDROGEN CONSUMPTION (SCFB)

FIGURE 7b

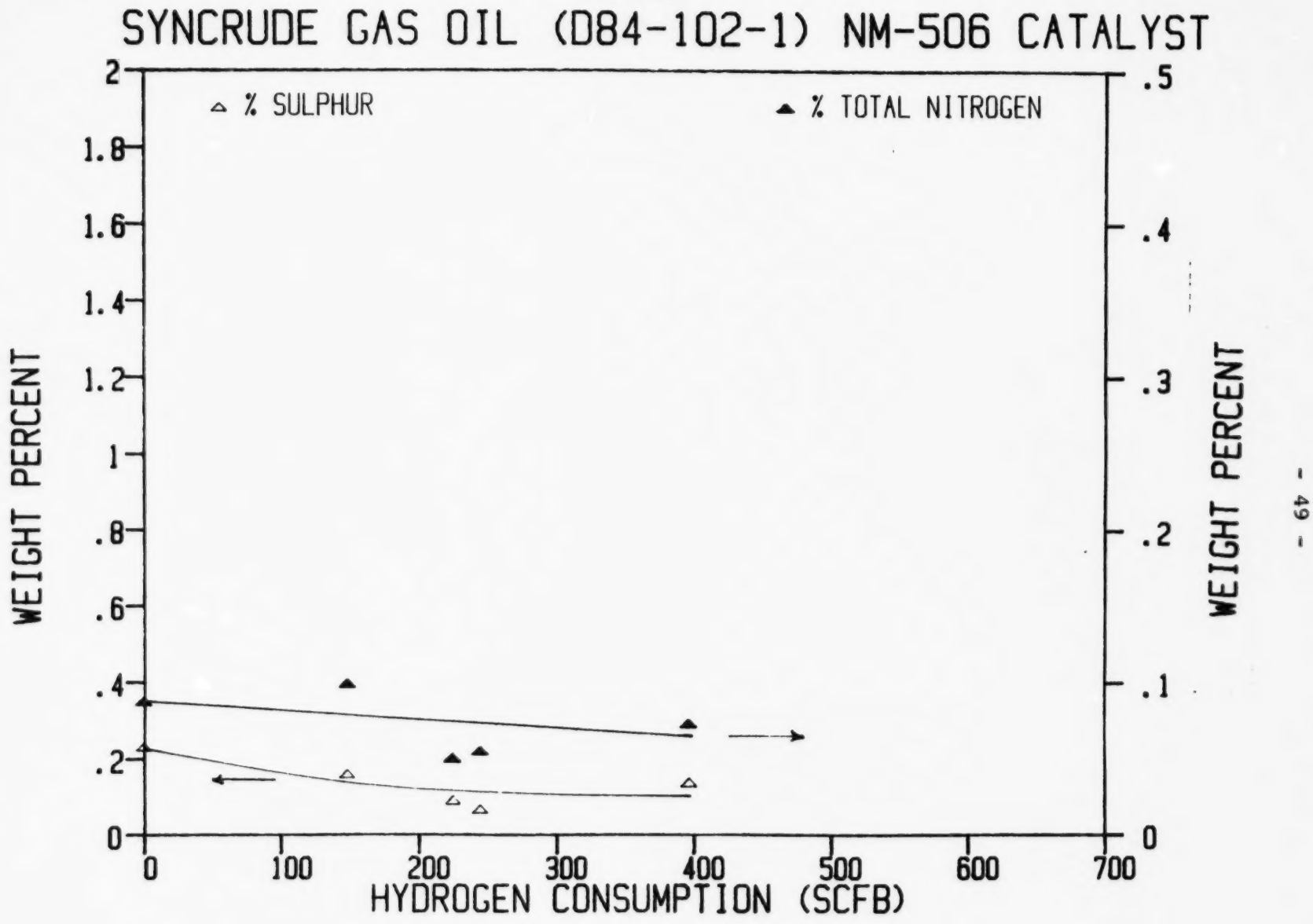

SYNCRUDE GAS OIL (D84-102-1) NM-506 CATALYST
△ % SULPHUR
▲ % TOTAL NITROGEN
WEIGHT PERCENT
WEIGHT PERCENT
2
1.8
1.6
1.4
1.2
1
.8
.6
.4
.2
0
.5
.4
.3
.2
.1
0
0
100
200
300
400
500
600
700
HYDROGEN CONSUMPTION (SCFB)

FIGURE 8a

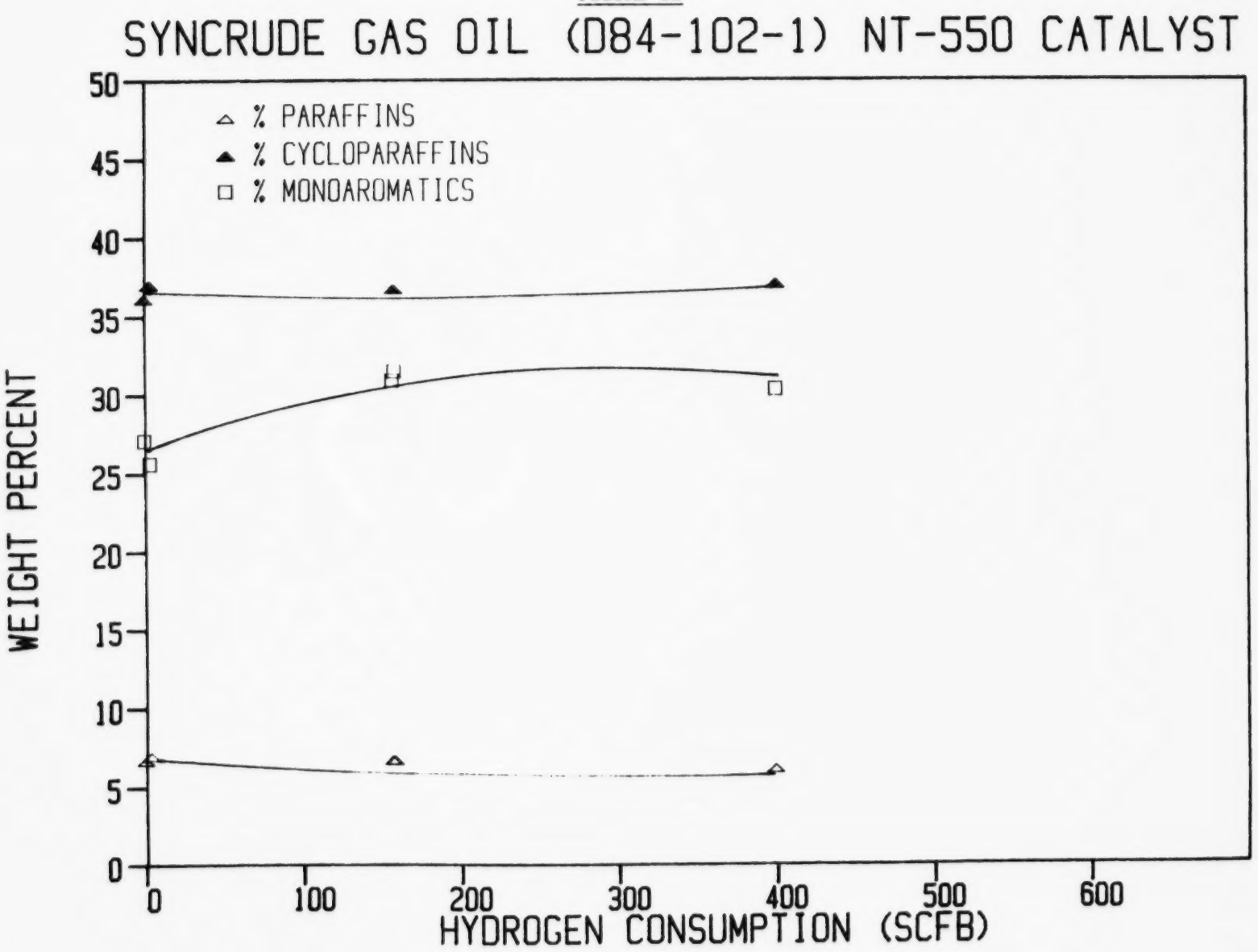

SYNCRUDE GAS OIL (D84-102-1) NT-550 CATALYST
△ % PARAFFINS
▲ % CYCLOPARAFFINS
□ % MONOAROMATICS
WEIGHT PERCENT
50
45
40
35
30
25
20
15
10
5
0
0
100
200
300
400
500
600
HYDROGEN CONSUMPTION (SCFB)

FIGURE 8b

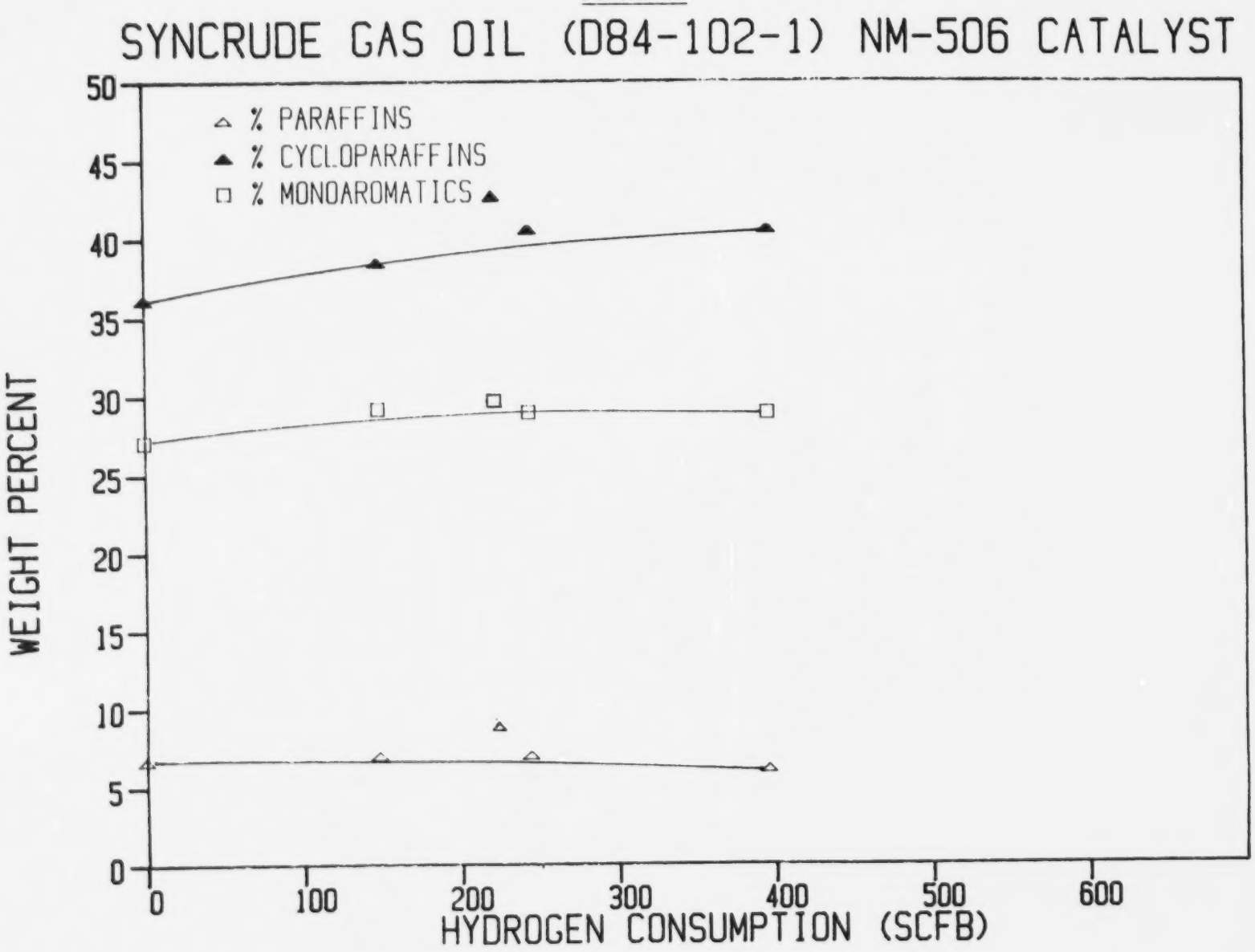

SYNCRUDE GAS OIL (D84-102-1) NM-506 CATALYST
% PARAFFINS
% CYCLOPARAFFINS
% MONOAROMATICS
WEIGHT PERCENT
0
5
10
15
20
25
30
35
40
45
50
0
100
200
300
400
500
600
HYDROGEN CONSUMPTION (SCFB)

FIGURE 9a

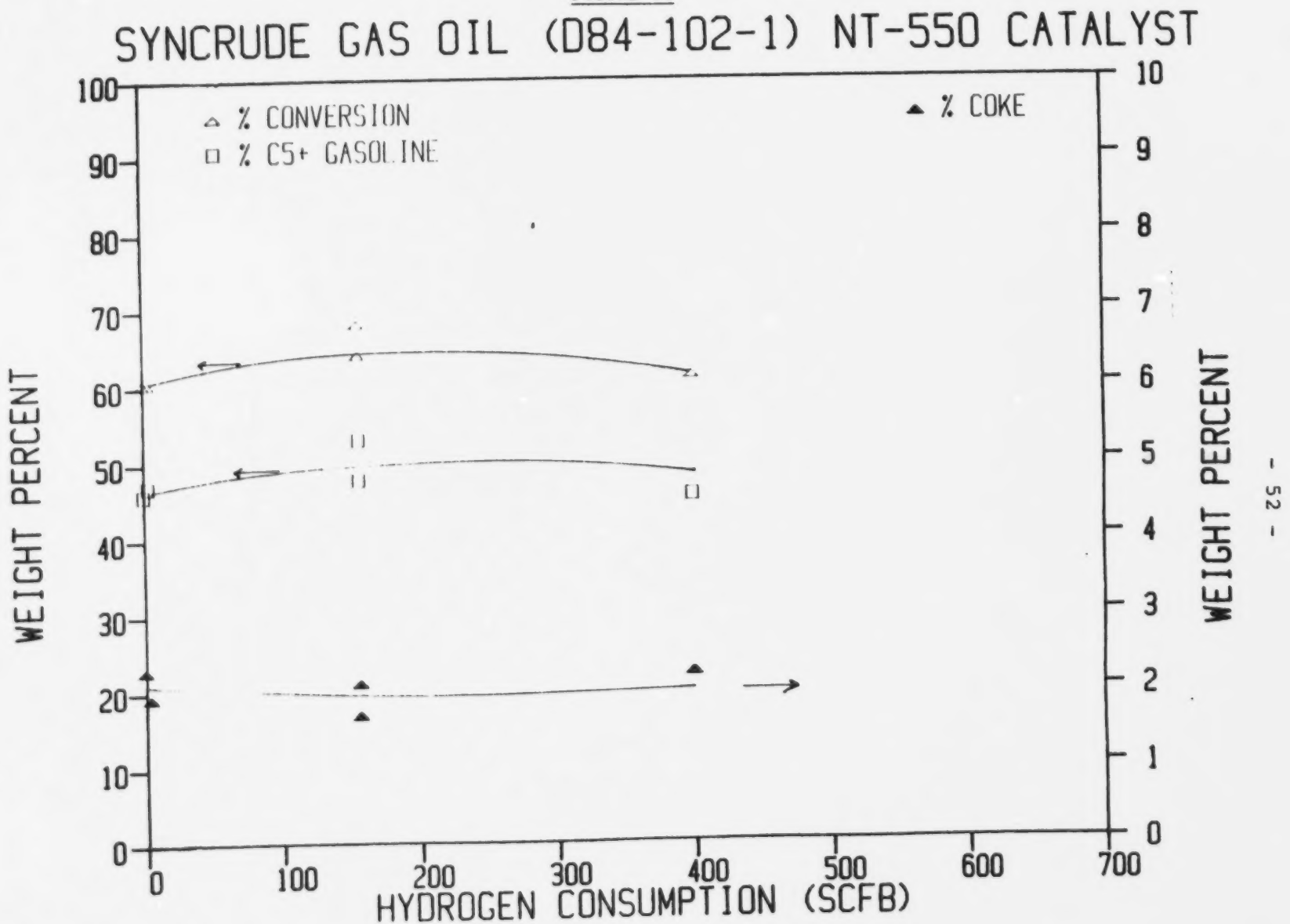
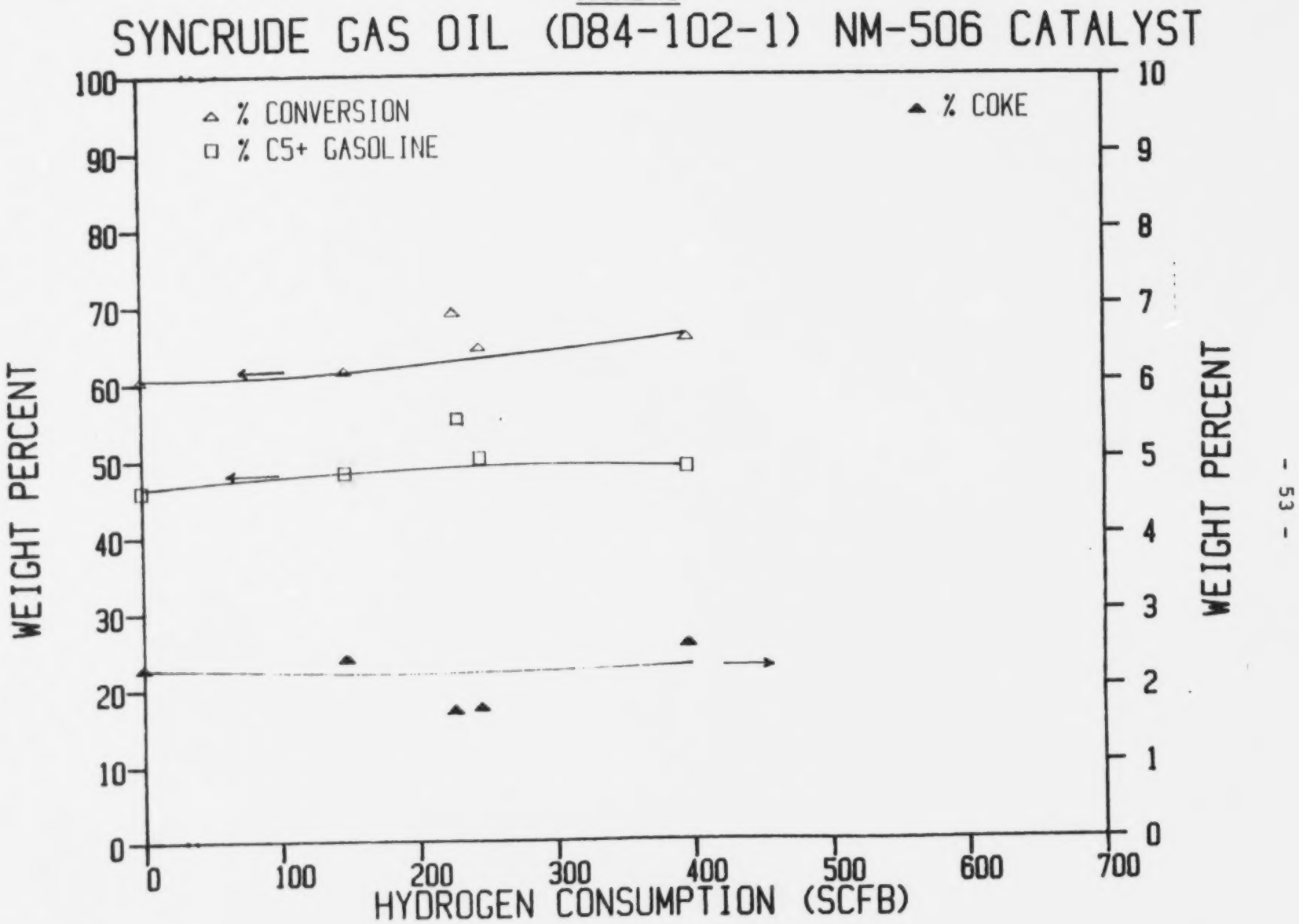

SYNCRUDE GAS OIL (D84-102-1) NT-550 CATALYST
% CONVERSION
% C5+ GASOLINE
% COKE
WEIGHT PERCENT
WEIGHT PERCENT
HYDROGEN CONSUMPTION (SCFB)
0
10
20
30
40
50
60
70
80
90
100
0
1
2
3
4
5
6
7
8
9
10
0
100
200
300
400
500
600
700

FIGURE 9b


SYNCRUDE GAS OIL (D84-102-1) NM-506 CATALYST
△ % CONVERSION
□ % C5+ GASOLINE
▲ % COKE
WEIGHT PERCENT
WEIGHT PERCENT
HYDROGEN CONSUMPTION (SCFB)
0
10
20
30
40
50
60
70
80
90
100
0
1
2
3
4
5
6
7
8
9
10
0
100
200
300
400
500
600
700

4. Suncor Gas Oil

Feed Evaluation

The feedstock data in Table 13 shows Suncor gas oil was very similar to the Syncrude feed with an API gravity of 23.3°, a total sulphur level of 0.33 wt.% and a total nitrogen level of 0.074 wt.%. Aniline point of Suncor (59.3°C) was slightly higher than Syncrude, indicating a lower aromatic content.

Coke forming tendency, as measured by Conradson carbon residue, was lower for Suncor (0.04 wt.%) than the Syncrude gas oil.

The distillation range shown in Table 14 had a 257°C 5% point, with a 443°C 90% boiling point. This gas oil contained slightly less heavy ends than the Syncrude.

The compositional data and fuel precursors in Table 15 show Suncor was similar to Lloydminster gas oil with 47.2% saturates, but more monoaromatics (24.8 wt.%) like the Syncrude oil. The cracking precursors were similar to the Syncrude and Lloydminster gas oils for gasoline yield and comparable to Rainbow Zama gas oil for light cycle oil, decant oil and coke yields.

Effect of Hydrogenation on Physical Properties

The hydrogenation study produced feedstocks (Table 13) which have the same trend as previous hydrogenated gas oils. API gravity and aniline point increased with hydrogen consumption, which was the result of a lowering of aromatic content by hydrogenation. Like the Syncrude gas oil, both catalysts were effective at reducing the aromatics, although NM-506 had a slight advantage with reaction condition #3 (343°C, 13.8 MPa, 2 LHSV).

Sulphur and nitrogen contents as a function of hydrogen consumption have been plotted in Figures 10a and 10b. Hydrogen consumption of 400 SCFB with NM-506 catalyst showed a noticeable reduction in both sulphur and nitrogen levels. The Syncrude gas, however, showed no significant reduction in either sulphur or nitrogen.

Conradson carbon residue results in Table 13 show that coking tendencies of Suncor gas oil were more sensitive to hydrogenation than Syncrude.

The Suncor feed, like Syncrude and Rainbow Zama gas oil feed, contained no metal poison (i.e. Ni, V). The higher Fe analysis for Run 15-44 was probably due to contamination of the sample during testing.

The GC analyses (Table 14) show the hydrogenation of Suncor gas oil did not significantly increase the level of lighter boiling material. Very little cracking or hydrogen substitution had occurred with hydrogenation.

Selected compositional data from Table 15 are plotted in Figures 11a and 11b.

Hydrogenation with both catalysts increased the cycloparaffins level; however, NM-506 catalyst was able to achieve the same increase with over 100 SCFB less hydrogen consumption than NT-550 catalyst.

Effects of Hydrogenation on Microactivity Tests (MAT)

As with the previous gas oils, catalyst to oil ratios did vary somewhat and so care must be used when comparing the MAT data. A comparison of selected MAT data versus hydrogen consumption is plotted in Figures 12a and 12b. Significant improvement in conversion, C_5+ gasoline and coke were only possible with NM-506 catalyst and 400 SCFB of hydrogen consumption. By comparison, Syncrude gas showed no change in MAT yields.

TABLE 13

Feedstock and Hydrogenated Product Characterization

Suncor Gas Oil (D84-88-1)

Hydrogenation Catalyst		NT 550	NT 550	NT 550	NT 550	NM 506	NM 506	NM 506	NM 506
Reaction Condition	Feed	#1	#2	#3	#4	#1	#2	#3	#4
		Run	Run	Run	Run	Run	Run	Run	Run
Characterization		15-18	15-19	15-21	15-20	15-41	15-42	15-44	15-43
Calculated Hydrogen Consumption SCFB		204	244	533	389	195	293	398	316
% Liquid Volume Yield		102	100	95	97	99	100	98	98
Density @ 15°C	0.9138	0.9092	0.9062	0.9025	0.9030	0.9077	0.9050	0.9001	0.9009
API Gravity	23.3	24.1	24.6	25.2	25.1	24.3	24.8	25.6	25.5
Aniline Pt, °C	59.3	58.8	58.8	63.2	60.3	60.0	61.0	64.7	62.9
Conradson Carbon, wt%	0.04	0.013	0.008	0.002	0.006	0.015	0.006	0.002	0.004
Basic Nitrogen, wt%	0.024	0.018	0.017	0.011	0.011	0.017	0.012	0.005	0.003
Total Nitrogen, wt%	0.074	0.079	0.065	0.031	0.049	0.070	0.052	0.017	0.025
Total Sulphur, wt%	0.33	0.13	0.09	0.06	0.04	0.12	0.08	0.05	0.01
cSt @ 40°C	12.92	12.21	12.20	12.81	10.86	11.94	12.12	12.02	11.20
cSt @ 100°C	2.82	2.73	2.73	2.82	2.57	2.71	2.73	2.73	2.62
VI	35	36	38	38	44	40	40	42	45
Metals µg/g									
Ni	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	(0.05
V	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	(0.05
Fe	2.1	0.15	0.22	0.56	0.40	0.11	0.16	2.6	0.46

Note:

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

TABLE 14

Feedstock and Hydrogenated Product Characterization

Suncor Gas Oil (D84-88-1)

Hydrogenation Catalyst Reaction Condition Characterization	Feed	NT 550 #1 Run 15-18	NT 550 #2 Run 15-19	NT 550 #3 Run 15-21	NT 550 #4 Run 15-20	NM 506 #1 Run 15-41	NM 506 #2 Run 15-42	NM 506 #3 Run 15-44	NM 506 #4 Run 15-43
G.C.Distillation, °C									
IBP	215	196	198	216	164	220	225	226	224
5%	257	250	250	256	240	252	252	251	250
10%	274	268	268	271	262	267	267	266	264
50%	349	344	343	344	339	343	340	337	336
90%	443	442	441	440	438	436	434	431	430
FBP	521	525	524	522	521	554	548	549	549

Note:

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

TABLE 15

Compositional Analysis of MAT Feeds

Suncor Gas Oil (D84-88-1)

Hydrogenation Catalyst		NT 550	NT 550	NT 550	NT 550	NM 506	NM 506	NM 506	NM 506
Reaction Condition / Run	Feed	#1 15-18	#2 15-19	#3 15-21	#4 15-20	#1 15-41	#2 15-42	#3 15-44	#4 15-43
Hydrocarbon Type, wt%									
Paraffins	11.00	11.25	10.89	11.06	11.13	12.61	12.58	11.23	11.41
Monocycloparaffins	10.89	13.90	11.26	15.68	14.87	11.86	12.17	15.27	15.07
Condensed Cycloparaffins	25.33	26.36	26.08	28.90	26.71	26.95	27.80	29.86	26.93
Alkylbenzenes	8.33	9.73	9.37	9.38	10.15	8.98	8.92	8.47	9.02
Benzocycloparaffins	9.41	9.54	11.60	10.17	11.00	9.83	10.97	10.60	11.17
Benzodicycloparaffins	7.07	7.12	10.20	10.08	9.53	7.69	9.45	10.05	9.59
Diaromatics	15.28	12.51	12.37	8.57	10.33	13.50	10.88	7.96	9.23
Triaromatics	4.88	4.10	3.08	1.86	2.74	4.05	2.62	1.81	2.75
Tetraaromatics	1.58	1.70	0.30	0.62	0.62	1.10	0.37	0.68	1.04
Polyaromatics & Polars	3.04	1.72	2.67	1.34	1.21	1.36	1.84	1.42	1.54
Aromatic Sulphur									
2-ring Compounds	1.55	0.98	0.83	0.60	0.68	1.09	1.00	1.07	1.00
3-ring Compounds	1.56	1.05	1.34	1.52	1.00	0.96	1.22	1.56	1.13
4-ring Compounds	0.07	0.04	0.00	0.20	0.03	0.01	0.17	0.20	0.10
Unidentified Hydrocarbons	0.01	0.00	0.01	0.02	0.00	0.01	0.01	0.00	0.02
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Precursors									
gas + gasoline	72.03	77.90	79.40	85.27	83.39	77.92	81.89	85.48	83.19
light cycle oil	17.61	14.02	13.87	9.93	11.51	15.07	12.49	9.81	10.79
decant oil + coke	10.36	8.08	6.73	4.80	5.10	7.01	5.62	4.71	6.02

Note:

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

TABLE 16

MAT Product Yield Data

Suncor Gas Oil (D84-88-1)

Hydrogenation Catalyst		NT 550	NT 550	NT 550	NT 550	NM 506	NM 506	NM 506	NM 506
Reaction Condition	Feed	#1	#2	#3	#4	#1	#2	#3	#4
Run	LC-27	LC-46	LC-101	LC-49	LC-48	LC-89	LC-90	LC-92	LC-91
Mass Balance, wt%	101.2	99.5	101.4	101.3	99.2	100.0	102.1	102.4	102.9
T, °C	489	490	489	490	490	490	490	490	490
C/O, g/g	4.01	4.21	3.94	4.04	4.27	3.88	3.78	3.98	3.99
Yields, wt% FF									
H_2	0.09	0.11	0.12	0.09	0.12	0.12	0.11	0.08	0.06
CH_4	0.27	0.30	0.30	0.28	0.32	0.30	0.28	0.27	0.24
$<C_2$	1.09	1.06	1.10	1.02	1.15	1.13	1.05	1.12	0.94
ΣC_3	4.32	4.94	4.82	5.16	5.45	4.72	4.74	4.74	4.67
ΣC_4	8.08	9.39	9.13	9.95	10.61	8.86	9.12	9.43	9.05
ΣC_5	4.11	4.77	5.32	4.85	5.72	4.94	4.98	5.74	5.11
C_5+ gasoline	47.69	49.02	52.21	55.55	53.40	49.17	52.69	57.11	54.48
C_6+ gasoline	43.57	44.24	46.88	50.69	47.68	44.22	47.71	51.36	49.37
LCO	27.25	26.05	24.57	21.94	22.27	26.52	23.92	20.77	23.32
DO	9.53	7.53	5.76	4.81	5.16	7.71	6.63	5.13	5.79
Coke	2.01	1.98	2.37	1.54	1.93	1.87	1.82	1.67	1.72
Conversion	63.20	66.41	69.66	73.24	72.56	65.76	69.43	74.08	70.88
C_6+ gasoline/Conversion	0.69	0.67	0.67	0.69	0.66	0.67	0.69	0.69	0.70
Coke/Conversion	0.03	0.03	0.03	0.02	0.03	0.03	0.03	0.02	0.02
C_6+ gasoline/coke	21.68	22.34	19.78	32.92	24.70	23.65	26.21	30.75	28.70

NOTE: All samples were cracked in the MAT reactor using DA 250 catalyst (MR3-19-1).

Note: Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

FIGURE 10a

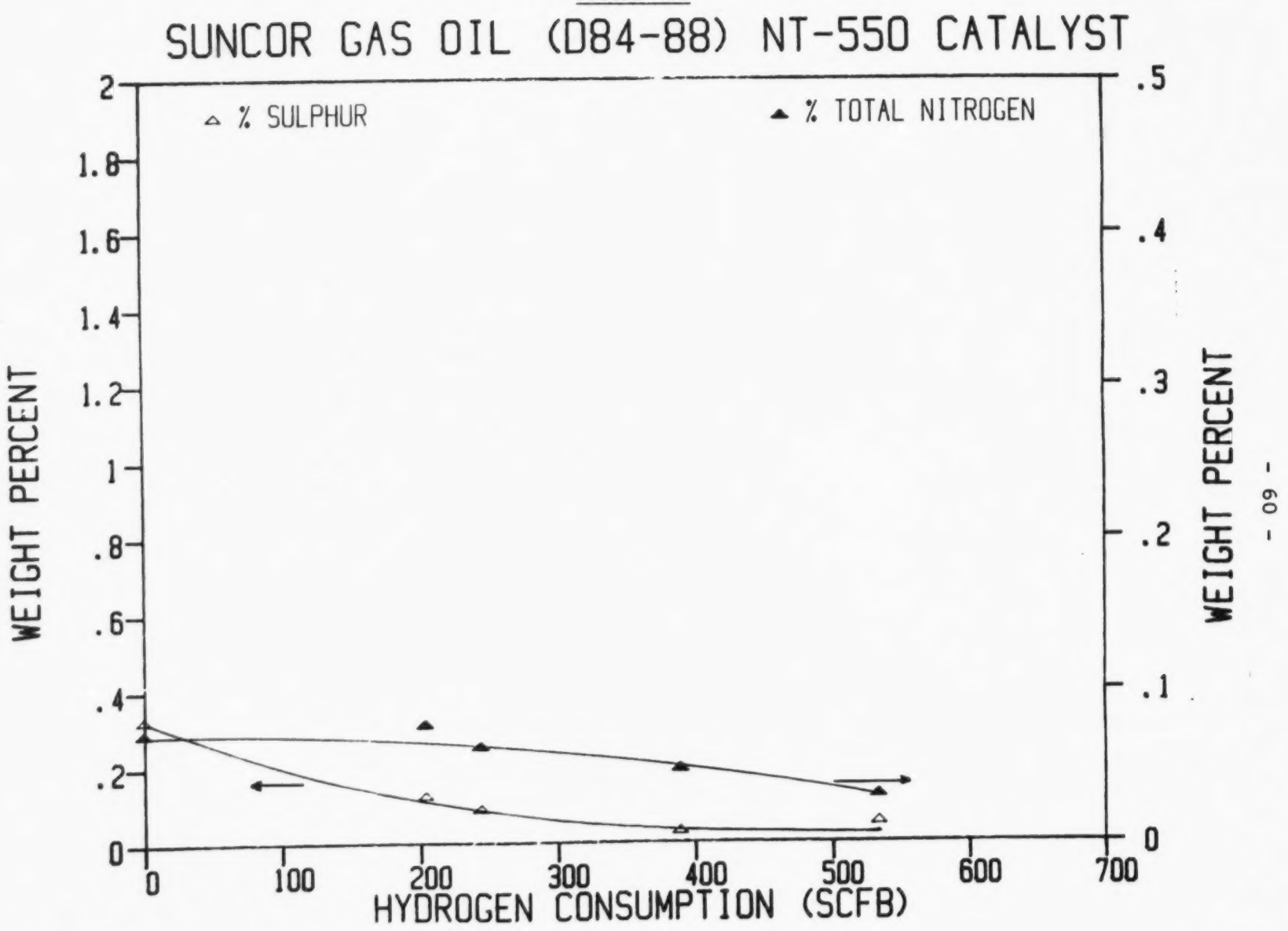

SUNCOR GAS OIL (D84-88) NT-550 CATALYST
△ % SULPHUR
▲ % TOTAL NITROGEN
WEIGHT PERCENT
WEIGHT PERCENT
HYDROGEN CONSUMPTION (SCFB)
0
.2
.4
.6
.8
1
1.2
1.4
1.6
1.8
2
0
.1
.2
.3
.4
.5
0
100
200
300
400
500
600
700

FIGURE 10b

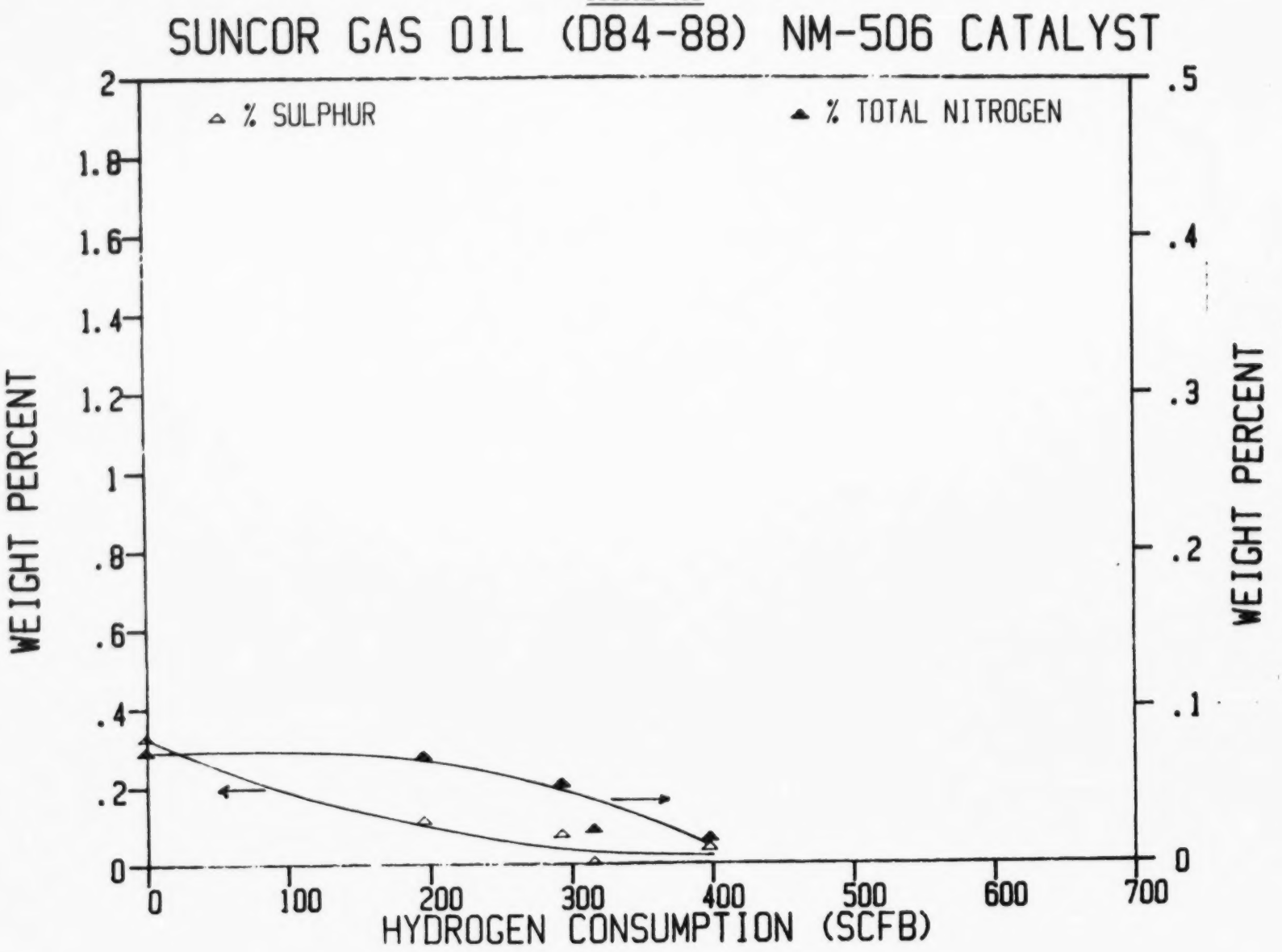

SUNCOR GAS OIL (D84-88) NM-506 CATALYST
△ % SULPHUR
▲ % TOTAL NITROGEN
WEIGHT PERCENT
WEIGHT PERCENT
2
1.8
1.6
1.4
1.2
1
.8
.6
.4
.2
0
.5
.4
.3
.2
.1
0
0
100
200
300
400
500
600
700
HYDROGEN CONSUMPTION (SCFB)

FIGURE 11a

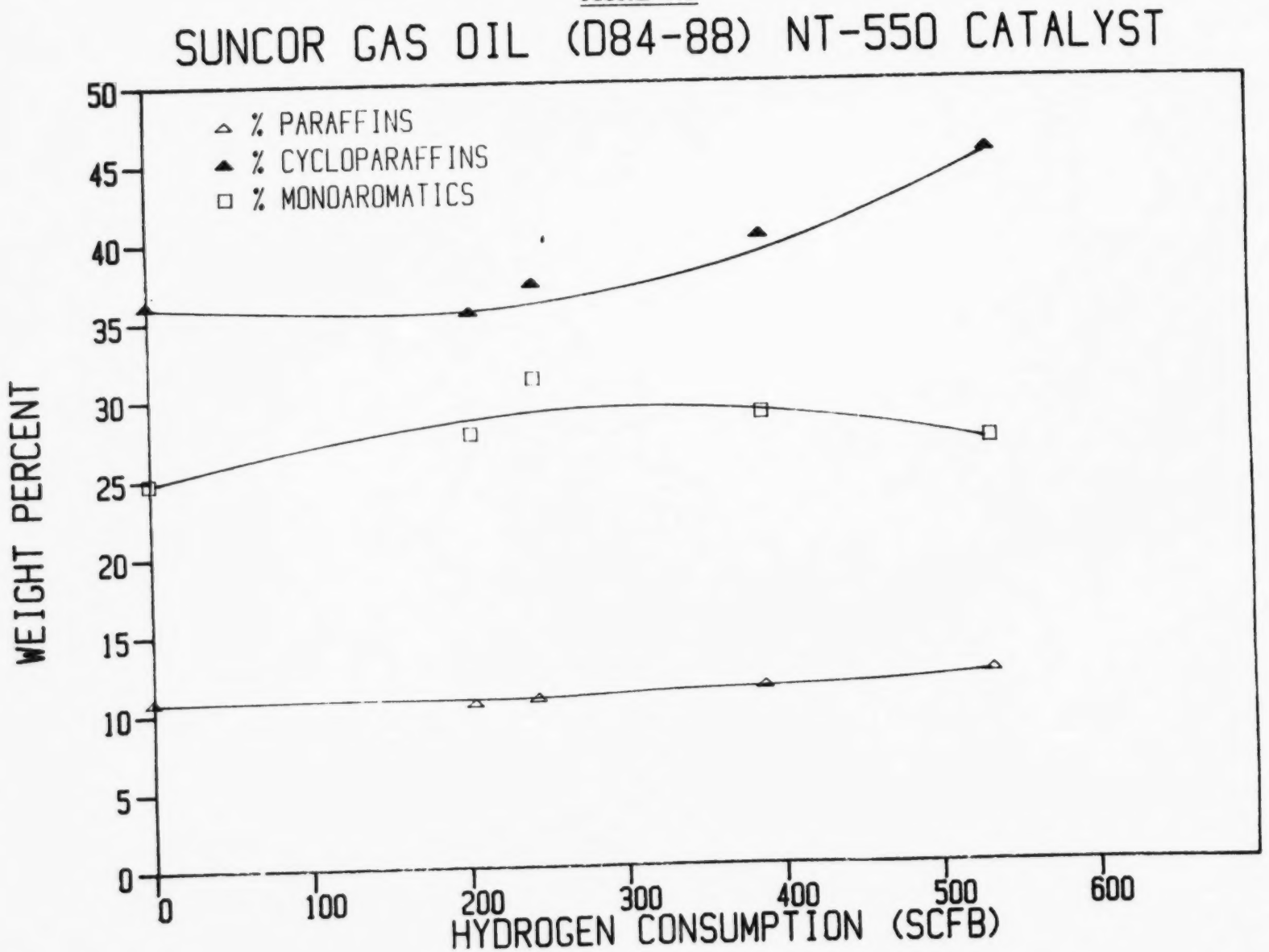

SUNCOR GAS OIL (D84-88) NT-550 CATALYST
% PARAFFINS
% CYCLOPARAFFINS
% MONOAROMATICS
WEIGHT PERCENT
0
5
10
15
20
25
30
35
40
45
50
0
100
200
300
400
500
600
HYDROGEN CONSUMPTION (SCFB)

FIGURE 11b

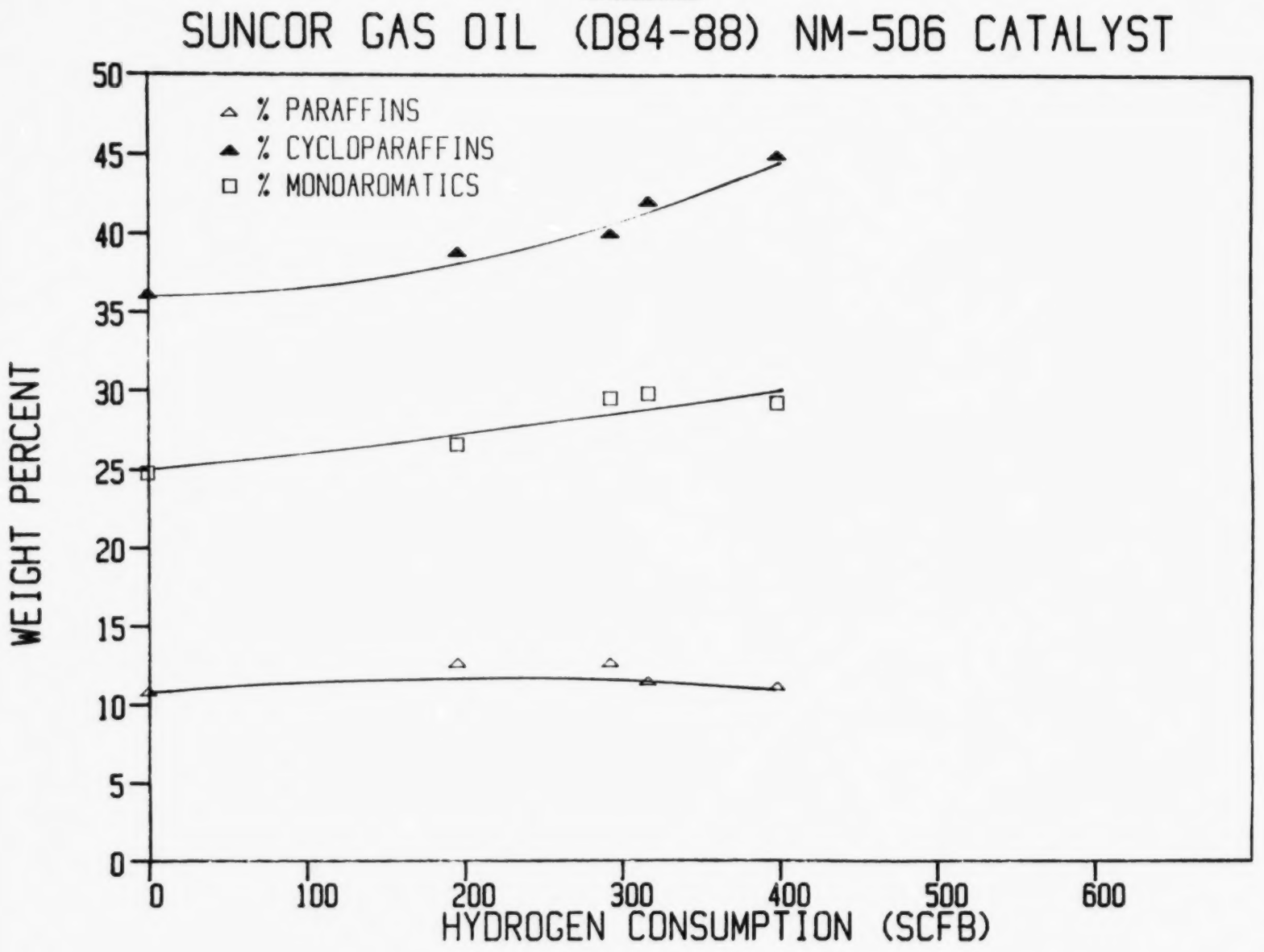

SUNCOR GAS OIL (D84-88) NM-506 CATALYST
% PARAFFINS
% CYCLOPARAFFINS
% MONOAROMATICS
WEIGHT PERCENT
0
5
10
15
20
25
30
35
40
45
50
0
100
200
300
400
500
600
HYDROGEN CONSUMPTION (SCFB)

FIGURE 12a

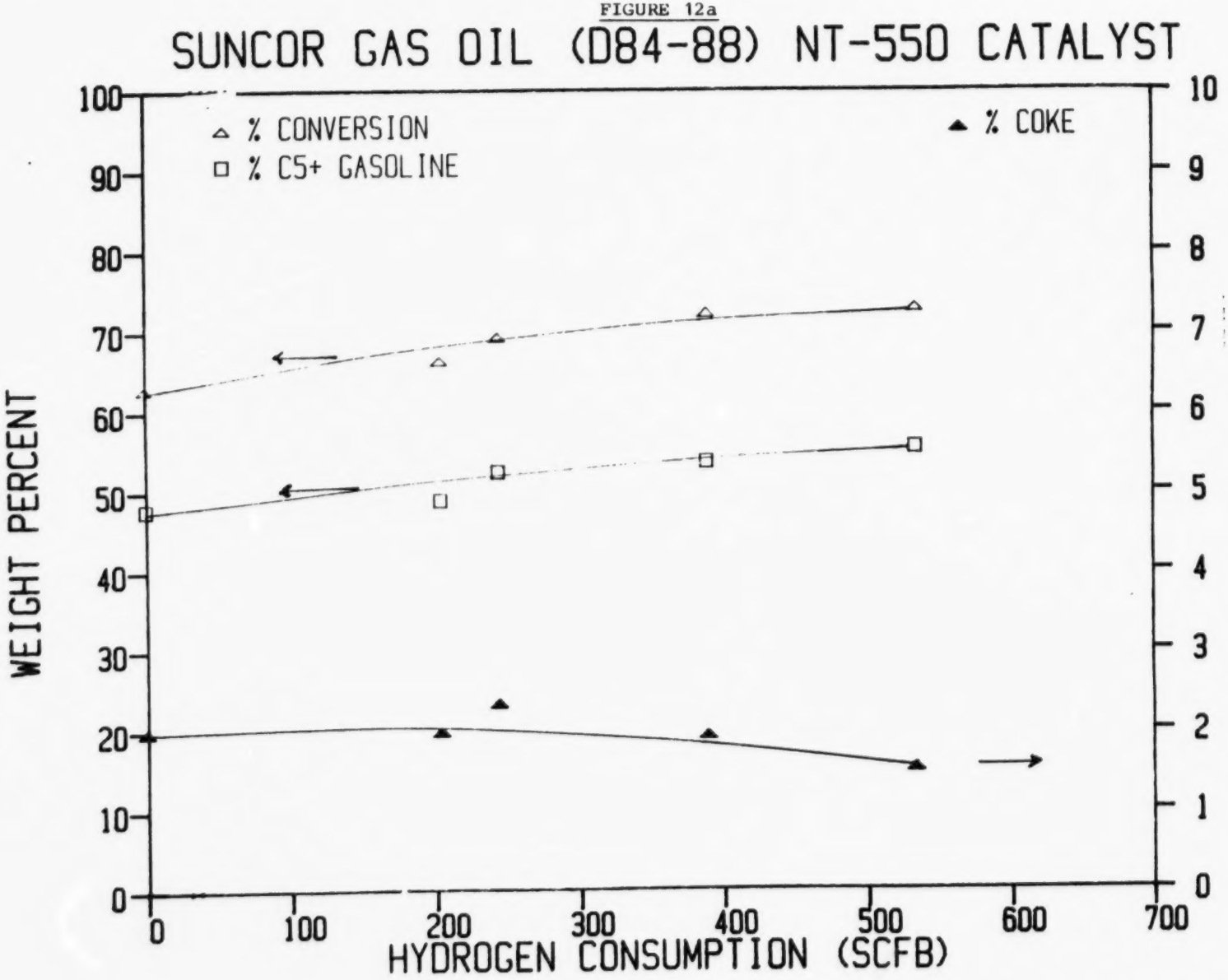
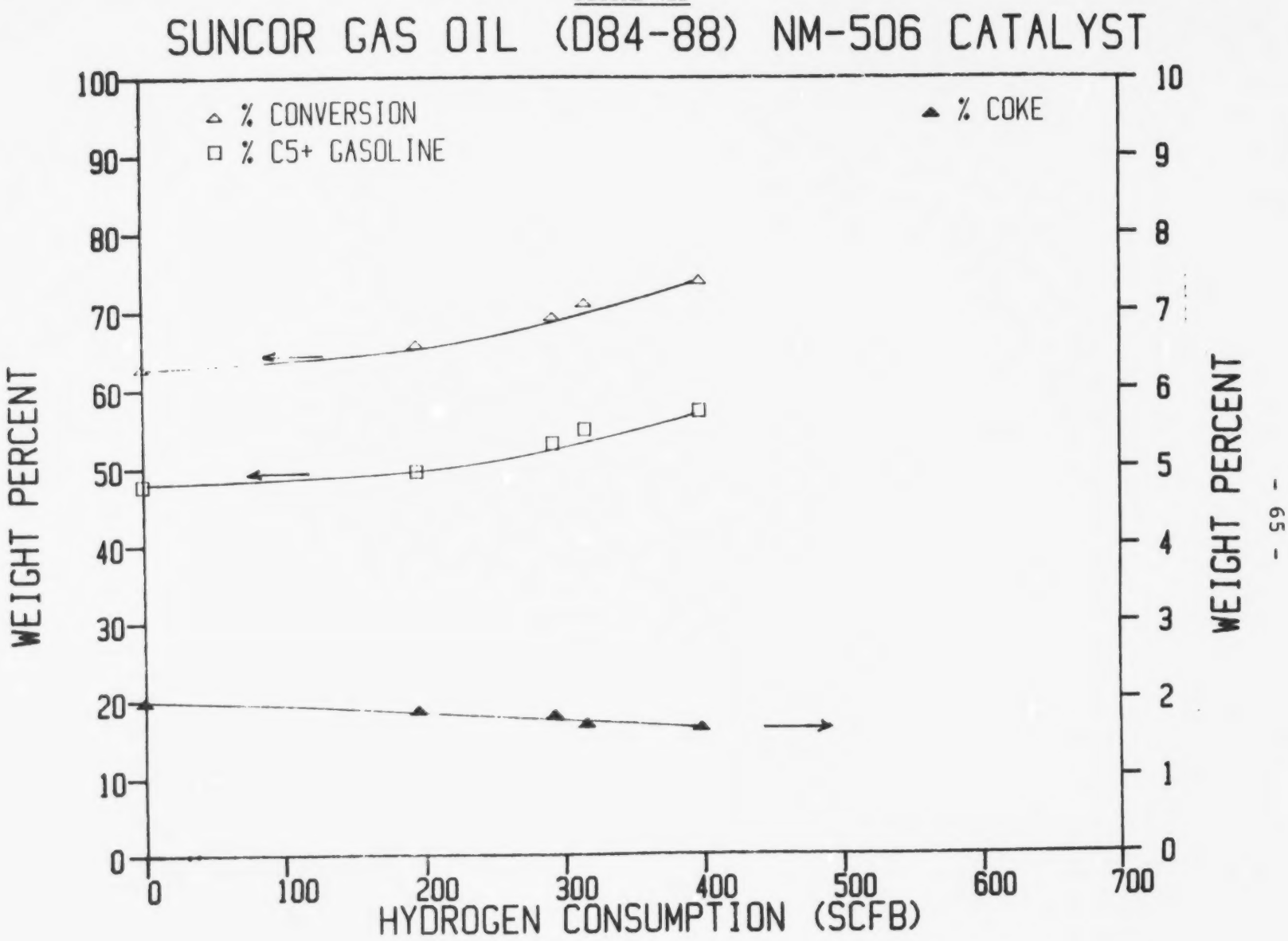

SUNCOR GAS OIL (D84-88) NT-550 CATALYST
△ % CONVERSION
□ % C5+ GASOLINE
▲ % COKE
WEIGHT PERCENT
WEIGHT PERCENT
HYDROGEN CONSUMPTION (SCFB)
0
10
20
30
40
50
60
70
80
90
100
0
1
2
3
4
5
6
7
8
9
10
0
100
200
300
400
500
600
700

FIGURE 12b


SUNCOR GAS OIL (D84-88) NM-506 CATALYST
% CONVERSION
% C5+ GASOLINE
% COKE
WEIGHT PERCENT
WEIGHT PERCENT
HYDROGEN CONSUMPTION (SCFB)
0
10
20
30
40
50
60
70
80
90
100
0
1
2
3
4
5
6
7
8
9
10
0
100
200
300
400
500
600
700

5. Edmonton Coker Gas Oil

Feed Evaluation

The feedstock data in Table 17 shows a typical Edmonton Coker gas oil has an API gravity similar to Lloydminster gas (22.3°) with a sulphur content similar to other gas oils in the study, but with the highest nitrogen level of any feedstock tested (0.163 wt.%). Aniline point is similar to Lloydminster gas oil (72.1°C).

Coke forming tendency, as measured by Conradson carbon residue, was low (0.04 wt.%) and similar to the Suncor gas oil.

The GC distillation range given in Table 18 had a 290°C 5% point and 427°C 90% boiling point. The 90% boiling point of the Edmonton Coker gas oil was lower than the other gas oils of the study.

The compositional analysis by mass spec (Table 19) could not differentiate between monocycloparaffins and olefins because they have the same molecular weight. Therefore, the higher saturates level (59.3 wt.%) may be due to some olefinic materials which cannot be distinguished from cycloparaffins.

Effect of Hydrogenation on Physical Properties

The characterization study of Edmonton Coker gas oil (Table 17) shows API gravity and aniline point increase with the mildest reaction condition. This is due to a reduction in the level of particularly unsaturates and aromatics with hydrogenation. Note that because of the deficiency of hydrogen in Edmonton Coker gas oil, the feed is quite sensitive even to Reaction Condition #1.

Sulphur and nitrogen results versus hydrogen consumption have been plotted in Figures 13a and 13b. Note that even the mildest reaction conditions allowed 400 SCFB of hydrogen consumption. The maximum reduction in sulphur and nitrogen levels was possible with NM-506 catalyst and condition #3.

Conradson carbon residues in Table 17 show even the mild reaction conditions reduced the carbon forming tendency significantly.

The Edmonton Coker gas oil, like the Suncor, Syncrude and Rainbow Zama feeds, contained no metal poisons (i.e. Ni, V).

The 5% and 90% points indicate no change occurred in the distillation range with hydrogenation. Selected compositional data from Table 19 are plotted in Figures 14a and 14b. NT-550 catalyst had the greatest effect on monoaromatics level with a reduced effect on paraffins level. NM-506 catalyst affected paraffins, cycloparaffins and monoaromatics levels. NM-506 also allowed greater hydrogen consumption than NT-550.

Reaction condition #3 with NM-506 gave the most gas + gasoline precursors, the least light cycle oil precursors and the least decant oil and coke precursors.

Effects of Hydrogenation on Microactivity Tests (MAT)

Since catalyst to oil ratios did vary somewhat, care must be used when comparing the MAT data.

A comparison of selected MAT data versus hydrogen consumption is plotted in Figures 15a and 15B.

Edmonton Coker gas oil had the lowest conversion of any feed tested before hydrogenation; however, with hydrogenation the level of conversion (74.5%) had increased beyond that of Rainbow Zama gas oil, which had the highest conversion of any gas oil before hydrogenation.

TABLE 17

Feedstock and Hydrogenated Product Characterization

Edmonton Coker Gas Oil (D85-7-1)

Hydrogenation Catalyst		NT 550	NT 550	NT 550	NT 550	NM 506	NM 506	NM 506	NM 506
Reaction Condition	Feed	#1	#2	#3	#4	#1	#2	#3	#4
		Run	Run	Run	Run	Run	Run	Run	Run
Characterization		15-23	15-24	15-26	15-25	15-46	15-47	15-49	15-48
Calculated Hydrogen Consumption SCFB		398	420	506	453	356	441	685	606
% Liquid Volume Yield		106	101	100	105	101	103	93*	101
Density @ 15°C	0.9194	0.8939	0.8920	0.8880	0.8885	0.8927	0.8892	0.8829	0.8849
API Gravity	22.3	26.7	27.0	27.8	27.7	26.9	27.6	28.7	28.3
Aniline Pt, °C	72.1	77.0	77.4	77.8	75.8	76.2	77.5	79.8	78.2
Conradson Carbon, wt%	0.04	0.007	0.004	0.002	<0.001	0.008	0.006	0.003	0.002
Basic Nitrogen, wt%	0.053	0.053	0.050	0.029	0.032	0.038	0.027	0.012	0.014
Total Nitrogen, wt%	0.163	0.141	0.123	0.086	0.104	0.093	0.079	0.034	0.065
Total Sulphur, wt%	0.44	0.15	0.11	0.09	0.06	0.13	0.09	0.04	0.03
cSt @ 40°C	11.88	11.23	11.49	11.32	10.76	11.06	11.07	10.84	10.45
cSt @ 100°C	2.85	2.77	2.81	2.80	2.71	2.76	2.76	2.74	2.68
VI	77	81	81	84	83	83	85	88	88
Metals µg/g									
Ni	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
V	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Fe	0.3	0.09	0.06	0.09	0.08	1.2	0.16	0.49	0.21

Note:

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

* Data should be considered suspect due to sampling error in the reactor.

TABLE 18

Feedstock and Hydrogenated Product Characterization

Edmonton Coker Gas Oil (D85-7-1)

Hydrogenation Catalyst Reaction Condition Characterization	Feed	NT 550 #1 Run 15-23	NT 550 #2 Run 15-24	NT 550 #3 Run 15-26	NT 550 #4 Run 15-25	NM 506 #1 Run 15-46	NM 506 #2 Run 15-47	NM 506 #3 Run 15-49	NM 506 #4 Run 15-48
G.C.Distillation, °C									
IBP	204	191	218	217	204	238	241	238	234
5%	290	273	278	275	266	284	282	274	273
10%	309	301	302	298	294	302	300	298	293
50%	366	363	362	361	359	362	361	356	356
90%	427	430	429	428	427	425	426	421	421
FBP	493	481	481	481	480	523	527	528	528

Note:

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

TABLE 19

Compositional Analysis of MAT Feeds

Edmonton Coker Gas Oil D85-7-1

Hydrogenation Catalyst		NT 550	NT 550	NT 550	NT 550	NM 506	NM 506	NM 506	NM 506
Reaction Condition	Feed	#1	#2	#3	#4	#1	#2	#3	#4
Run		15-23	15-24	15-26	15-25	15-46	15-47	15-49	15-48
Hydrocarbon Type, wt%									
Paraffins	27.00	31.13	30.77	31.25	30.72	30.79	31.04	33.34	33.22
Monocycloparaffins	13.49	12.51	12.75	13.12	13.08	13.27	13.58	14.08	13.76
Condensed Cycloparaffins	18.82	17.70	18.01	19.60	18.74	17.92	18.65	21.98	20.91
Alkylbenzenes	4.94	4.96	5.06	4.77	5.01	5.54	4.92	3.92	3.84
Benzocycloparaffins	4.22	5.30	6.02	6.22	6.33	5.69	6.34	5.45	5.25
Benzodicycloparaffins	3.73	4.91	6.77	8.27	8.01	4.89	6.99	8.62	7.57
Diaromatics	12.44	12.88	11.40	9.32	10.60	11.97	10.20	7.71	9.24
Triaromatics	5.94	5.34	4.39	2.99	3.39	5.00	3.62	1.73	2.79
Tetraaromatics	2.39	1.52	0.83	0.39	0.64	1.57	0.79	0.26	0.38
Polyaromatics & Polars	4.26	1.88	2.01	2.12	1.63	1.74	2.09	0.93	1.47
Aromatic Sulphur									
2-ring Compounds	1.09	0.53	0.58	0.39	0.45	0.56	0.47	0.36	0.29
3-ring Compounds	1.46	1.23	1.36	1.44	1.32	1.05	1.22	1.50	1.21
4-ring Compounds	0.20	0.09	0.04	0.11	0.05	0.01	0.08	0.12	0.07
Unidentified Hydrocarbons	0.02	0.02	0.01	0.01	0.03	0.00	0.01	0.02	0.00
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Precursors									
gas + gasoline	72.20	76.51	79.38	83.23	81.89	78.10	81.52	87.37	84.55
light cycle oil	14.26	14.03	12.66	10.43	11.71	13.06	11.28	8.82	10.14
decant oil + coke	13.54	9.46	7.96	6.34	6.40	8.84	7.20	3.81	5.31

Note:

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

TABLE 20

MAT Product Yield Data

Edmonton Coker Gas Oil D85-7-1

Hydrogenation Catalyst		NT 550	NT 550	NT 550	NT 550	NM 506	NM 506	NM 506	NM 506
Reaction Condition	Feed	#1	#2	#3	#4	#1	#2	#3	#4
Run	LC-32	LC-51	LC-103	LC-54	LC-53	LC-94	LC-95	LC-97	LC-96
Mass Balance, wt%	101.9	101.8	100.0	104.6	101.9	101.4	102.0	100.0	97.57
T, °C	491	490	490	490	489	490	490	490	490
C/O, g/g	4.24	4.20	3.96	4.36	4.21	3.61	4.02	3.90	4.06
Yields, wt% FF									
H_2	0.08	0.11	0.14	0.08	0.09	0.13	0.10	0.08	0.13
CH_4	0.31	0.29	0.31	0.24	0.27	0.22	0.25	0.27	0.33
$<C_2$	1.11	0.96	1.07	0.81	0.93	0.81	0.88	0.93	1.27
C_3	3.84	4.33	5.07	4.50	4.60	3.71	4.34	5.53	5.38
C_4	7.03	8.00	9.26	8.94	8.58	6.88	8.34	10.94	10.76
C_5	4.01	4.57	5.33	5.51	4.59	3.68	4.63	6.14	7.17
C_5^+ gasoline	40.12	44.47	46.50	51.60	48.06	41.67	47.33	55.50	51.72
C_6^+ gasoline	36.10	39.89	41.16	46.09	43.46	37.99	42.69	49.36	44.55
LCO	28.26	27.56	25.20	23.06	25.07	27.46	25.79	20.33	21.78
DO	16.81	12.33	10.50	8.96	10.70	17.46	11.40	5.13	7.11
Coke	2.81	2.32	2.39	2.10	2.03	1.96	1.90	1.60	1.96
Conversion	54.92	60.09	64.30	67.97	64.21	55.06	62.80	74.52	71.10
C_6^+ gasoline/Conversion	0.66	0.66	0.64	0.68	0.68	0.69	0.68	0.66	0.63
Coke/Conversion	0.05	0.04	0.04	0.03	0.03	0.04	0.03	0.02	0.03
C_6^+ gasoline/coke	12.85	17.19	17.22	21.95	21.41	19.38	22.47	30.85	22.73

NOTE: All samples were cracked in the MAT reactor using DA 250 catalyst (MR3-19-1).

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#1	343	2.76	2
#2	343	5.51	2
#3	343	13.78	2
#4	343	5.51	1

FIGURE 13a

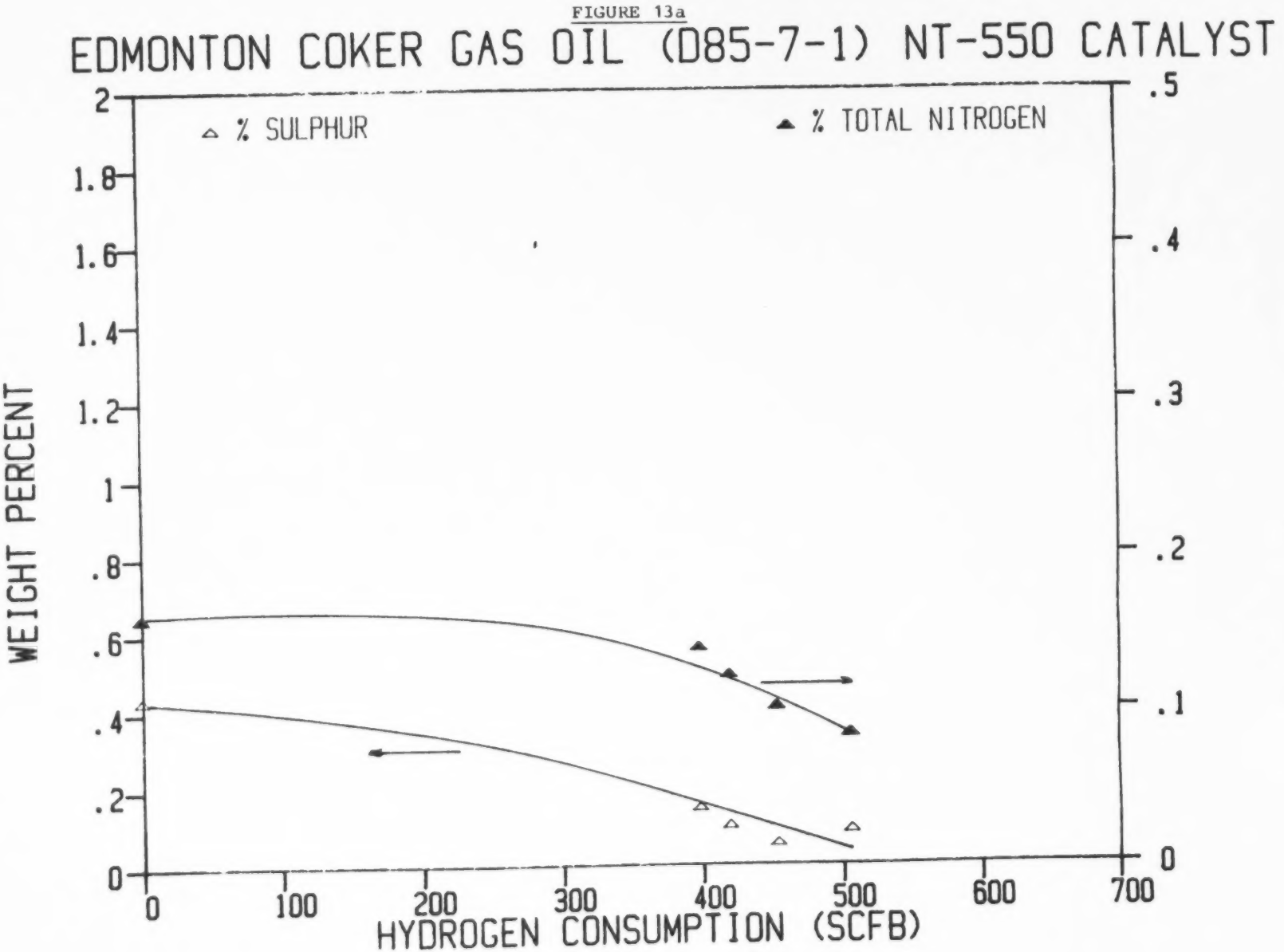

EDMONTON COKER GAS OIL (D85-7-1) NT-550 CATALYST
△ % SULPHUR
▲ % TOTAL NITROGEN
WEIGHT PERCENT
2
1.8
1.6
1.4
1.2
1
.8
.6
.4
.2
0
.5
.4
.3
.2
.1
0
0
100
200
300
400
500
600
700
HYDROGEN CONSUMPTION (SCFB)

FIGURE 13b

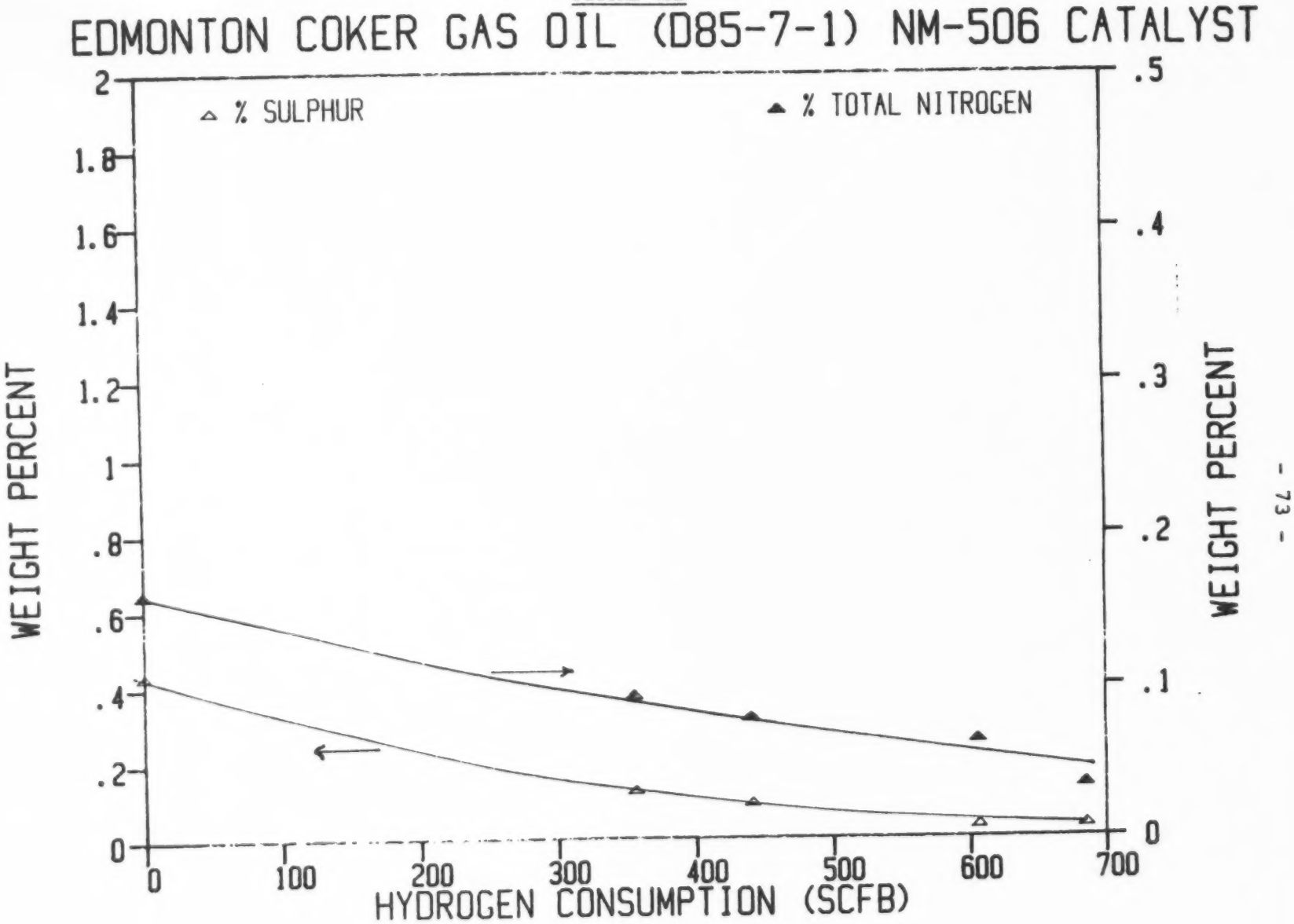

EDMONTON COKER GAS OIL (D85-7-1) NM-506 CATALYST
% SULPHUR
% TOTAL NITROGEN
WEIGHT PERCENT
WEIGHT PERCENT
2
1.8
1.6
1.4
1.2
1
.8
.6
.4
.2
0
.5
.4
.3
.2
.1
0
0
100
200
300
400
500
600
700
HYDROGEN CONSUMPTION (SCFB)

FIGURE 14a

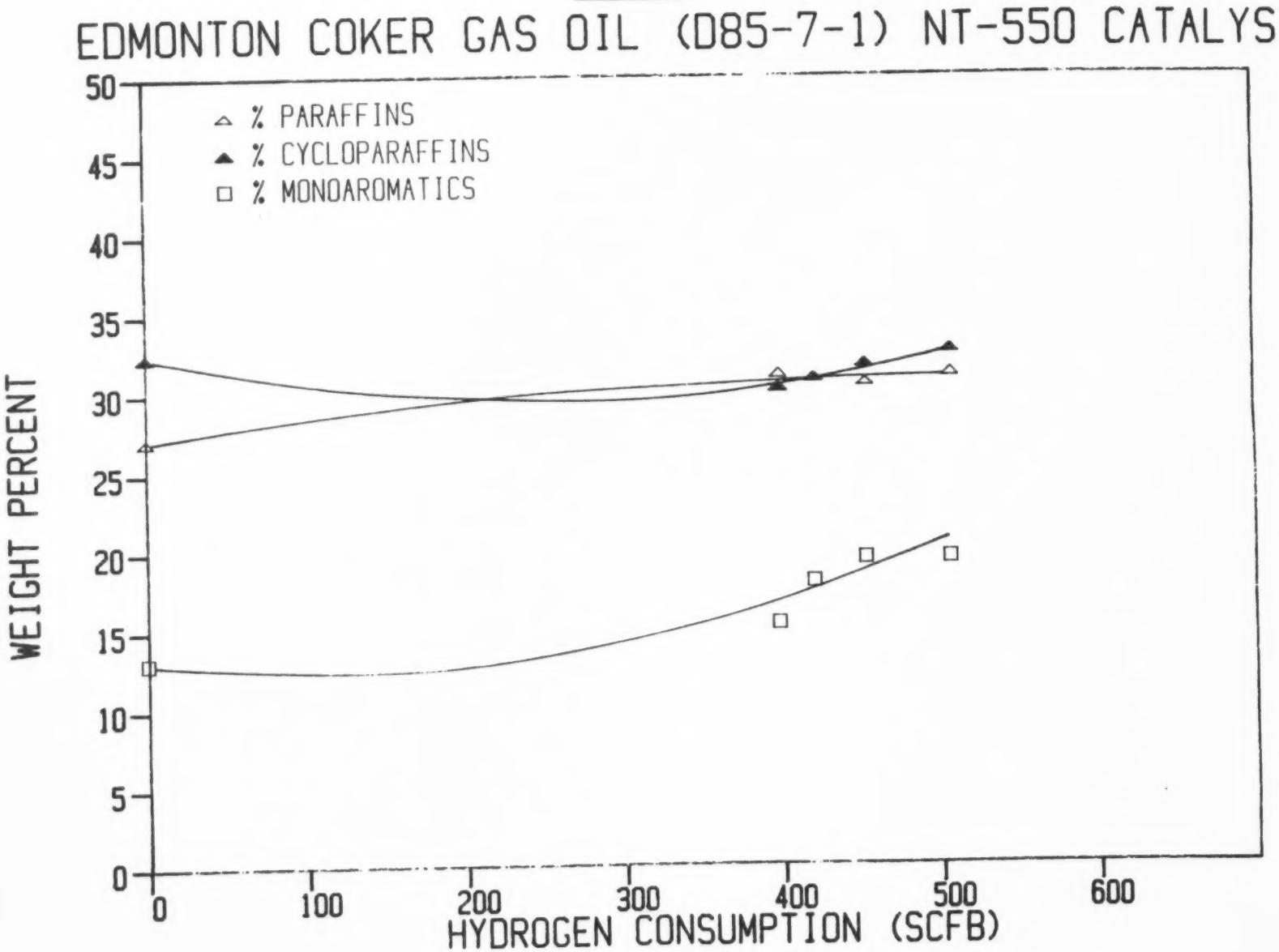

EDMONTON COKER GAS OIL (D85-7-1) NT-550 CATALYST
% PARAFFINS
% CYCLOPARAFFINS
% MONOAROMATICS
WEIGHT PERCENT
0
5
10
15
20
25
30
35
40
45
50
0
100
200
300
400
500
600
HYDROGEN CONSUMPTION (SCFB)

FIGURE 14b

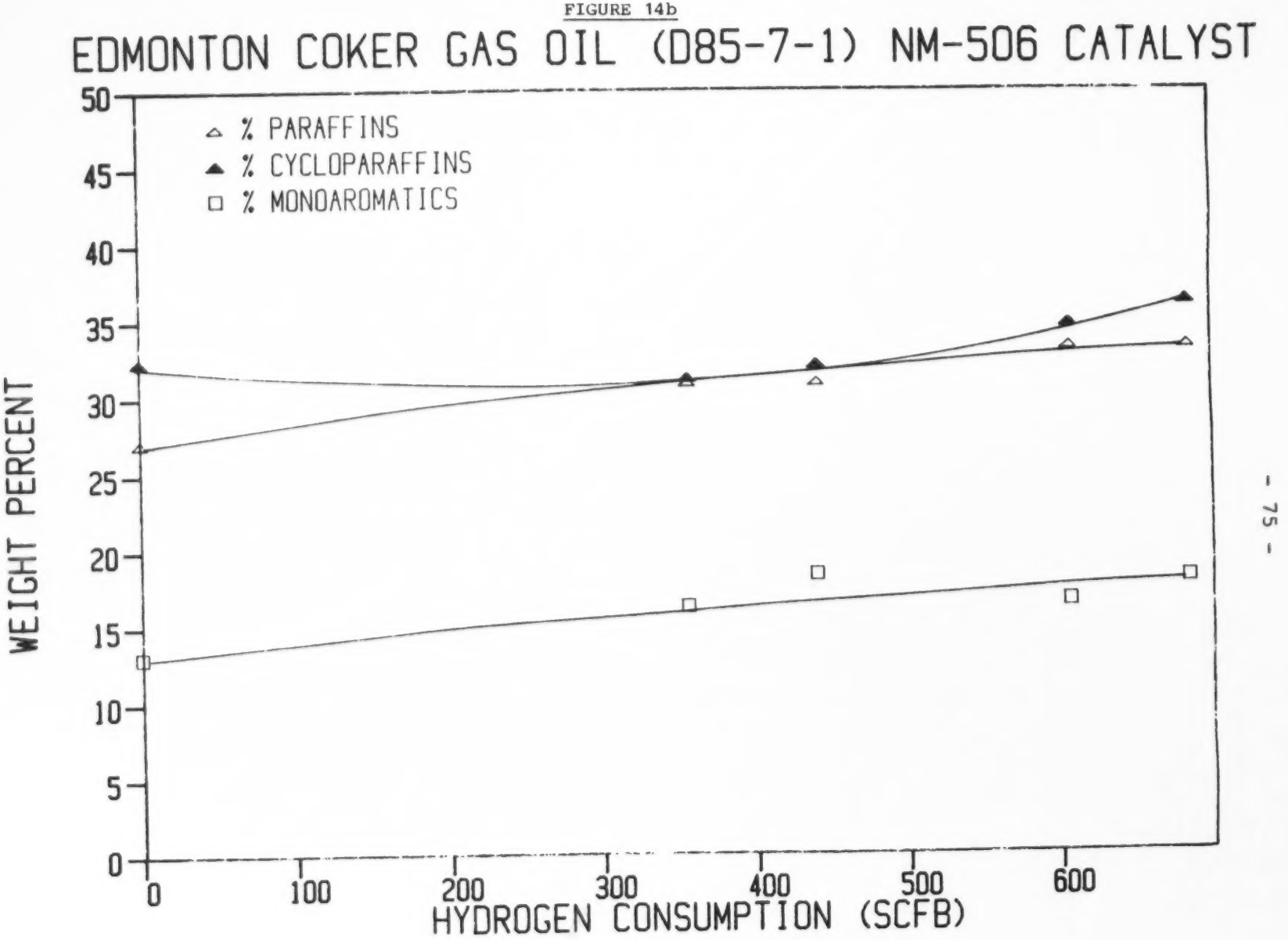

EDMONTON COKER GAS OIL (D85-7-1) NM-506 CATALYST
% PARAFFINS
% CYCLOPARAFFINS
% MONOAROMATICS
WEIGHT PERCENT
0
5
10
15
20
25
30
35
40
45
50
0
100
200
300
400
500
600
HYDROGEN CONSUMPTION (SCFB)

FIGURE 15a

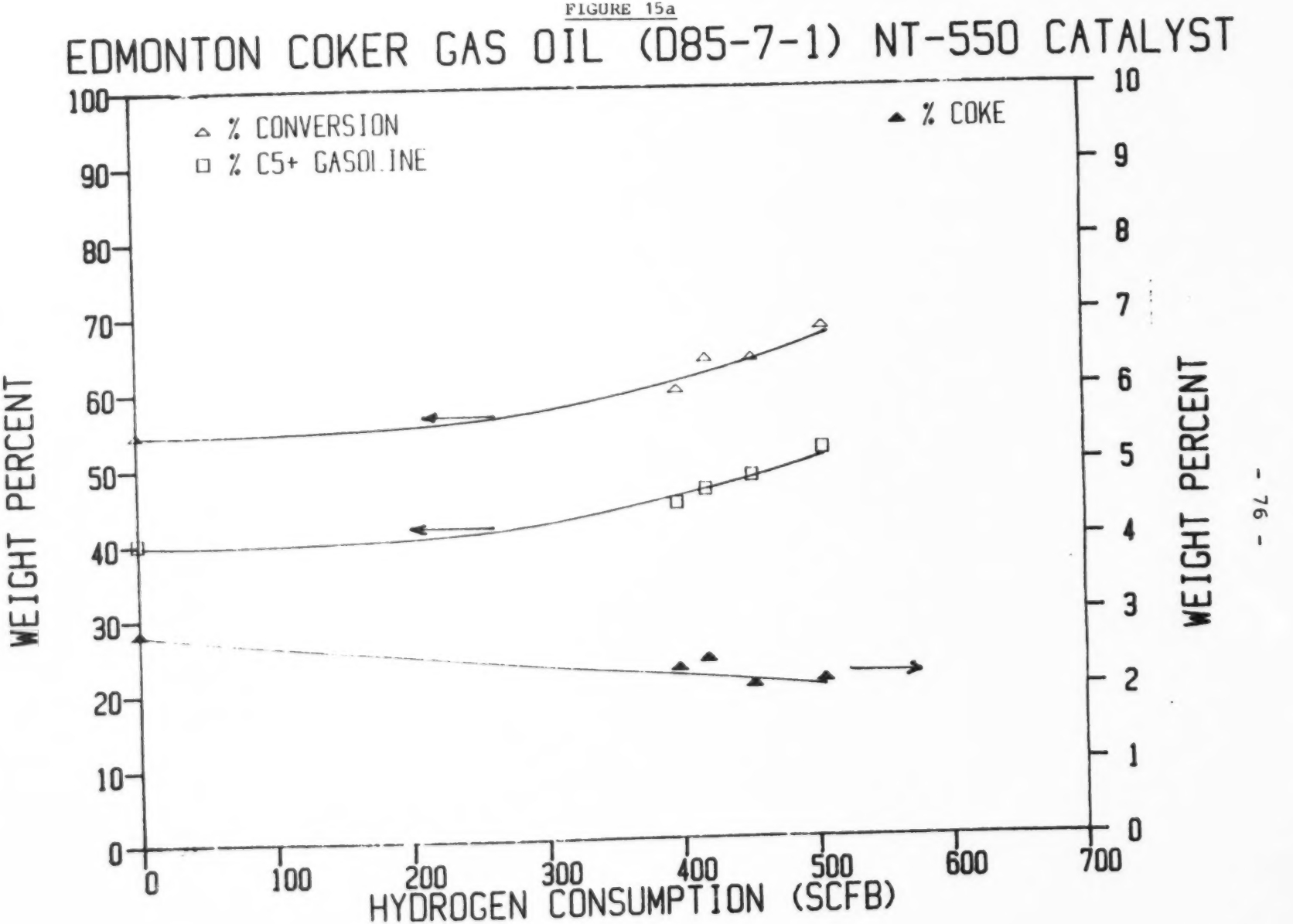
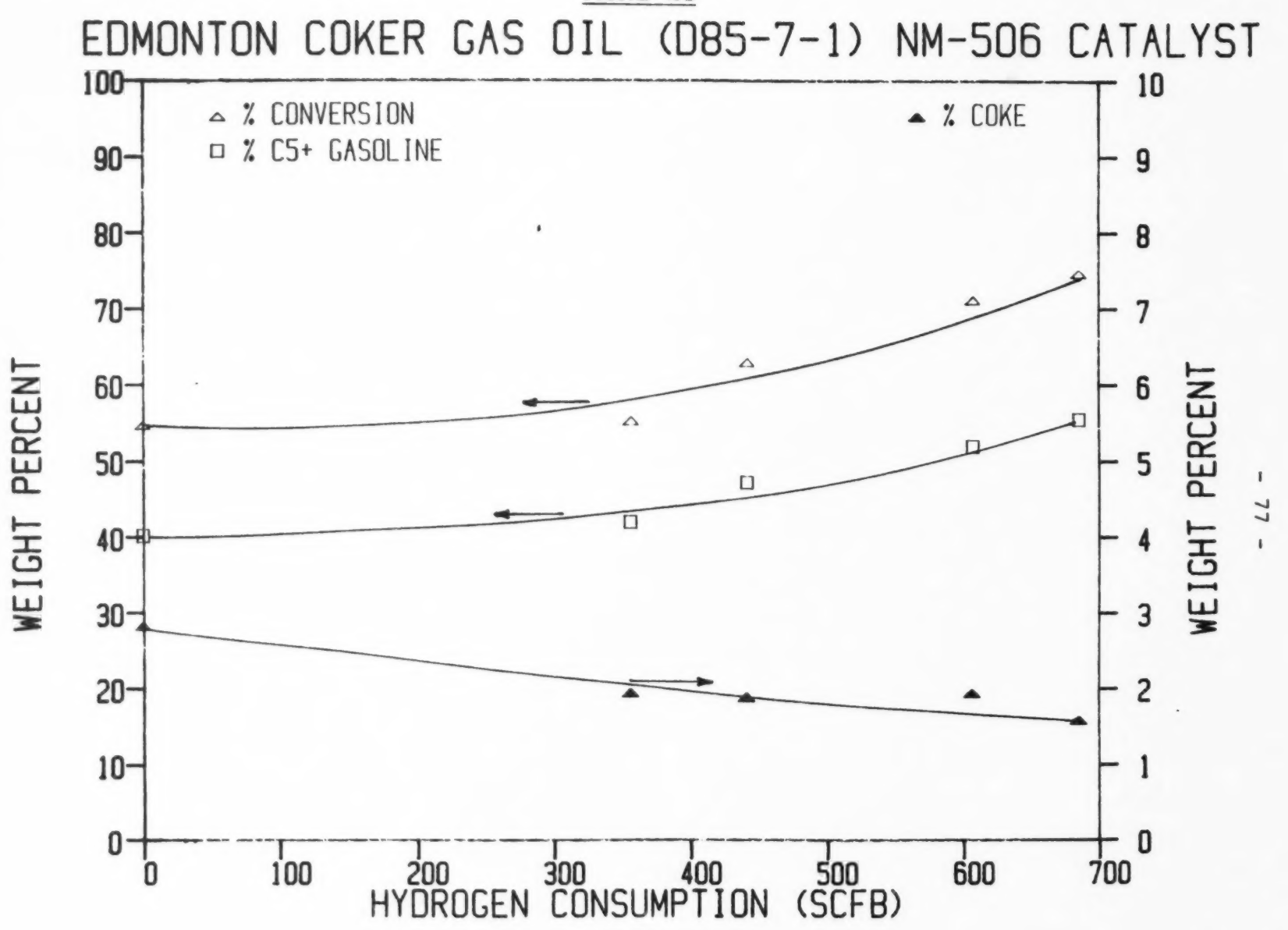

EDMONTON COKER GAS OIL (D85-7-1) NT-550 CATALYST
△ % CONVERSION
□ % C5+ GASOLINE
▲ % COKE
WEIGHT PERCENT
WEIGHT PERCENT
HYDROGEN CONSUMPTION (SCFB)
0
10
20
30
40
50
60
70
80
90
100
0
1
2
3
4
5
6
7
8
9
10
0
100
200
300
400
500
600
700

FIGURE 15b


EDMONTON COKER GAS OIL (D85-7-1) NM-506 CATALYST
△ % CONVERSION
□ % C5+ GASOLINE
▲ % COKE
WEIGHT PERCENT
WEIGHT PERCENT
HYDROGEN CONSUMPTION (SCFB)
0
10
20
30
40
50
60
70
80
90
100
0
1
2
3
4
5
6
7
8
9
10
0
100
200
300
400
500
600
700

6. "Standard" Gas Oil

Before any hydrogenation work had been started, a decision was made to run a standard gas oil feed periodically during the series of hydrogenations to monitor any activity loss in the catalysts. Lloydminster gas oil was selected as the standard and run at the reaction condition most likely to show degradation of the catalyst; condition #3.

Characterization studies (Table 21) show the catalysts' ability to remove sulphur and nitrogen compounds remained constant for the study. Nitrogen and sulphur levels for each standard run have been plotted in Figure 16a.

GC analyses (Table 22) show almost no change in the distillation results throughout the study.

Compositional analyses (Table 23) show the amount of gas and gasoline precursors produced did not vary significantly throughout the study. Selected compositional data have been plotted in Figure 16b.

MAT product yield data (Table 24) shows conversion of the standard remained fairly constant when the variations from catalyst to oil ratio are considered. Selected MAT data have been plotted in Figure 16c.

TABLE 21

Feedstock and Hydrogenated Product Characterization

Lloydminster Gas Oil "Standard" D85-8-1

Hydrogenation Catalyst		NT 550	NT 550	NT 550	NM 506	NM 506	NM 506
Reaction Condition	Feed	#3	#3	#3	#3	#3	#3
Run		15-13	15-22	15-27	15-40	15-45	15-50
Characteristics							
% Liquid Volume Yield		104	104	97	99	102	100
Density @ 15°C	0.9238	0.8999	0.8993	0.8997	0.8951	0.8952	0.8943
API Gravity	21.6	25.6	25.8	25.7	26.5	26.6	26.7
Aniline Point, °C	66.1	74.2	75.2	74.5	77.5	77.4	77.9
Conradson Carbon, wt%	0.09	0.002	0.007	0.005	0.009	0.005	0.007
Basic Nitrogen, wt%	0.019	0.011	0.010	0.008	0.005	0.004	0.003
Total Nitrogen, wt%	0.049	0.028	0.027	0.024	0.010	0.009	0.008
Total Sulphur, wt%	2.03	0.25	0.23	0.24	0.13	0.13	0.12
cSt @ 40°C	28.89	21.59	21.07	21.23	20.29	20.70	19.73
cSt @ 100°C	4.48	2.75	3.84	3.85	3.77	3.79	3.71
VI	34	78	46	46	50	45	51
Metals, µg/g							
Ni	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
V	0.18	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Fe	2.2	0.06	0.21	0.05	0.60	0.53	0.27

Note:

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#3	343	13.78	2

TABLE 22

Feedstock and Hydrogenated Product Characterization

Lloydminster Gas Oil "Standard" D85-8-1

Hydrogenation Catalyst		NT 550	NT 550	NT 550	NM 506	NM 506	NM 506
Reaction Condition Run	Feed	#3 15-13	#3 15-22	#3 15-27	#3 15-40	#3 15-45	#3 15-50
G.C.D.							
IBP	250	223	209	222	237	236	235
5%	307	282	280	280	280	279	278
10%	329	304	302	302	300	299	299
50%	394	380	379	378	375	375	374
90%	466	460	458	458	450	449	449
FBP	552	548	545	549	560	561	574

Note:

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#3	343	13.78	2

TABLE 23

Compositional Analysis of MAT Feeds

Lloydminster Gas Oil "Standard" D85-8-1

Hydrogenation Catalyst		NT 550	NT 550	NT 550	NM 506	NM 506	NM 506
Reaction Condition		#3	#3	#3	#3	#3	#3
Run	Feed	15-13	15-22	15-27	15-40	15-45	15-50
Hydrocarbon Type, wt%							
Paraffins	14.21	16.79	17.33	17.29	16.97	18.03	17.96
Monocycloparaffins	11.16	13.43	14.47	13.62	14.54	14.59	14.53
Condensed Cycloparaffins	22.39	26.82	28.48	27.62	31.50	31.62	31.50
Alkylbenzenes	5.94	8.90	8.68	8.52	7.87	7.76	7.34
Benzocycloparaffins	6.11	7.75	7.22	7.67	8.09	7.30	7.61
Benzodicycloparaffins	6.08	6.93	6.95	7.03	7.79	7.17	7.55
Diaromatics	15.29	8.90	8.97	9.12	7.48	7.47	7.27
Triaromatics	5.46	2.56	2.48	2.50	1.35	1.45	1.46
Tetraaromatics	2.74	1.18	1.00	1.21	0.75	1.03	0.90
Polyaromatics & Polars	3.32	3.22	1.78	2.15	1.17	1.10	1.03
Aromatic Sulphur							
2-ring Compounds	3.64	0.82	0.55	0.89	0.84	0.66	0.94
3-ring Compounds	2.96	1.96	1.92	2.03	1.47	1.55	1.63
4-ring Compounds	0.38	0.20	0.08	0.13	0.14	0.06	0.15
Unidentified Hydrocarbons	0.32	0.54	0.09	0.22	0.04	0.21	0.13
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Precursors							
gas + gasoline	65.89	80.62	83.13	81.75	86.76	86.47	86.49
light cycle oil	20.41	10.70	10.48	11.03	9.06	8.91	9.03
decant oil + coke	13.70	8.68	6.39	7.22	4.18	4.62	4.48

Note:

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#3	343	13.78	2

TABLE 24

MAT Product Yield Data

Lloydminster Gas Oil "Standard" D85-8-1

Hydrogenation Catalyst		NT 550	NT 550	NT 550	NM 506	NM 506	NM 506
Reaction Condition	Feed	#3	#3	#3	#3	#3	#3
Run	LC-31	LC-41	LC-50	LC-55	LC-88	LC-93	LC-98
Mass Balance, wt%	101.4	100.9	103.1	101.1	101.1	100.7	103.3
T, °C	489	490	490	489	490	490	490
C/O, g/g	4.21	4.16	4.24	4.17	4.06	3.91	3.95
Yields, wt% FF							
H_2	0.06	0.00	0.13	0.07	0.08	0.07	0.08
CH_4	0.36	0.30	0.27	0.26	0.28	0.30	0.27
$<C_2$	2.03	1.00	0.99	0.93	0.96	1.10	0.97
ΣC_3	4.92	5.24	5.20	4.89	5.41	5.24	5.23
ΣC_4	9.24	10.42	10.60	10.09	11.44	10.95	10.57
ΣC_5	4.92	5.00	5.72	5.26	6.56	6.19	5.79
C_5+ gasoline	47.60	53.30	56.20	54.52	58.30	58.05	59.58
C_6+ gasoline	42.68	48.29	50.48	49.26	51.74	51.86	53.78
LCO	23.28	21.64	19.04	20.43	17.45	17.95	17.72
DO	10.36	6.58	5.68	7.11	4.70	5.07	4.24
Coke	2.54	1.79	2.26	2.01	1.71	1.61	1.66
Conversion	66.34	71.77	75.27	72.45	77.48	76.97	78.03
C_6+ gasoline/Conversion	0.64	0.67	0.67	0.68	0.66	0.67	0.69
Coke/Conversion	0.04	0.03	0.03	0.03	0.02	0.02	0.02
C_6+ gasoline/coke	16.80	26.98	22.33	24.51	30.26	32.21	32.40

NOTE: All samples were cracked in the MAT reactor using DA 250 catalyst (MR3-19-1).

Reaction Condition	Temperature °C	Pressure MPa	Space Velocity h^{-1}
#3	343	13.78	2

FIGURE 16a

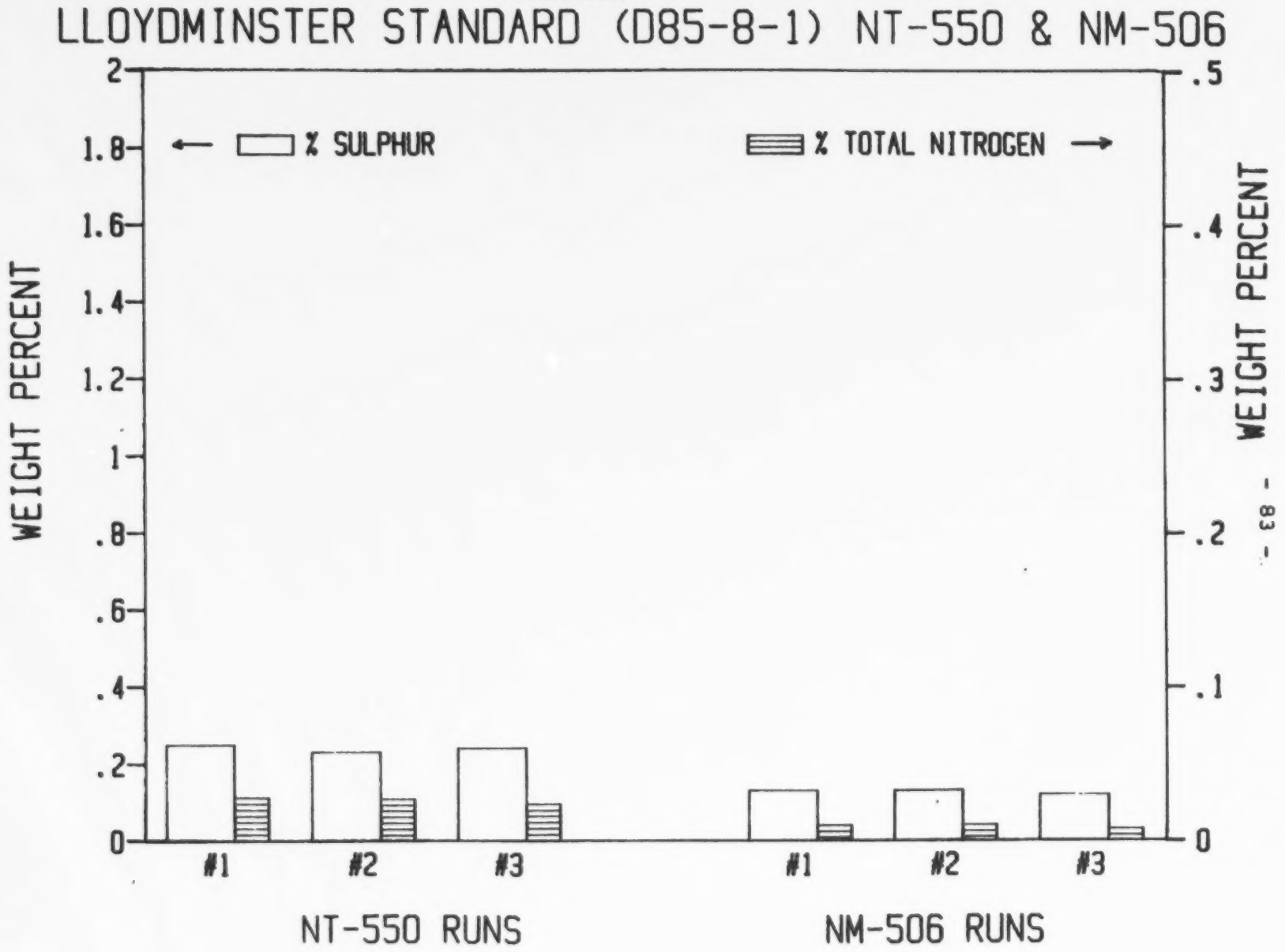

LLOYDMINSTER STANDARD (D85-8-1) NT-550 & NM-506
% SULPHUR
% TOTAL NITROGEN
WEIGHT PERCENT
WEIGHT PERCENT
2
1.8
1.6
1.4
1.2
1
.8
.6
.4
.2
0
.5
.4
.3
.2
.1
0
#1
#2
#3
#1
#2
#3
NT-550 RUNS
NM-506 RUNS

FIGURE 16b

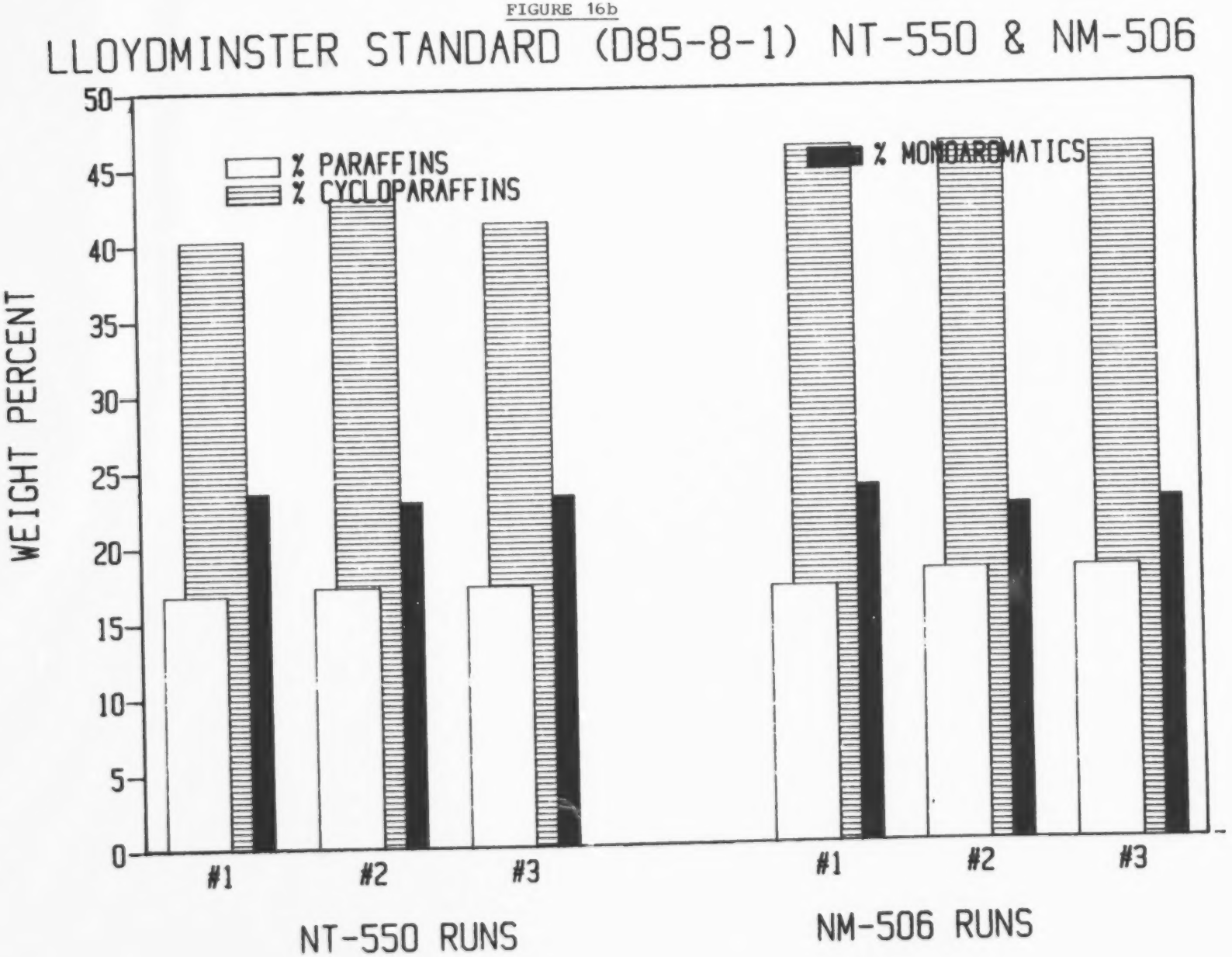
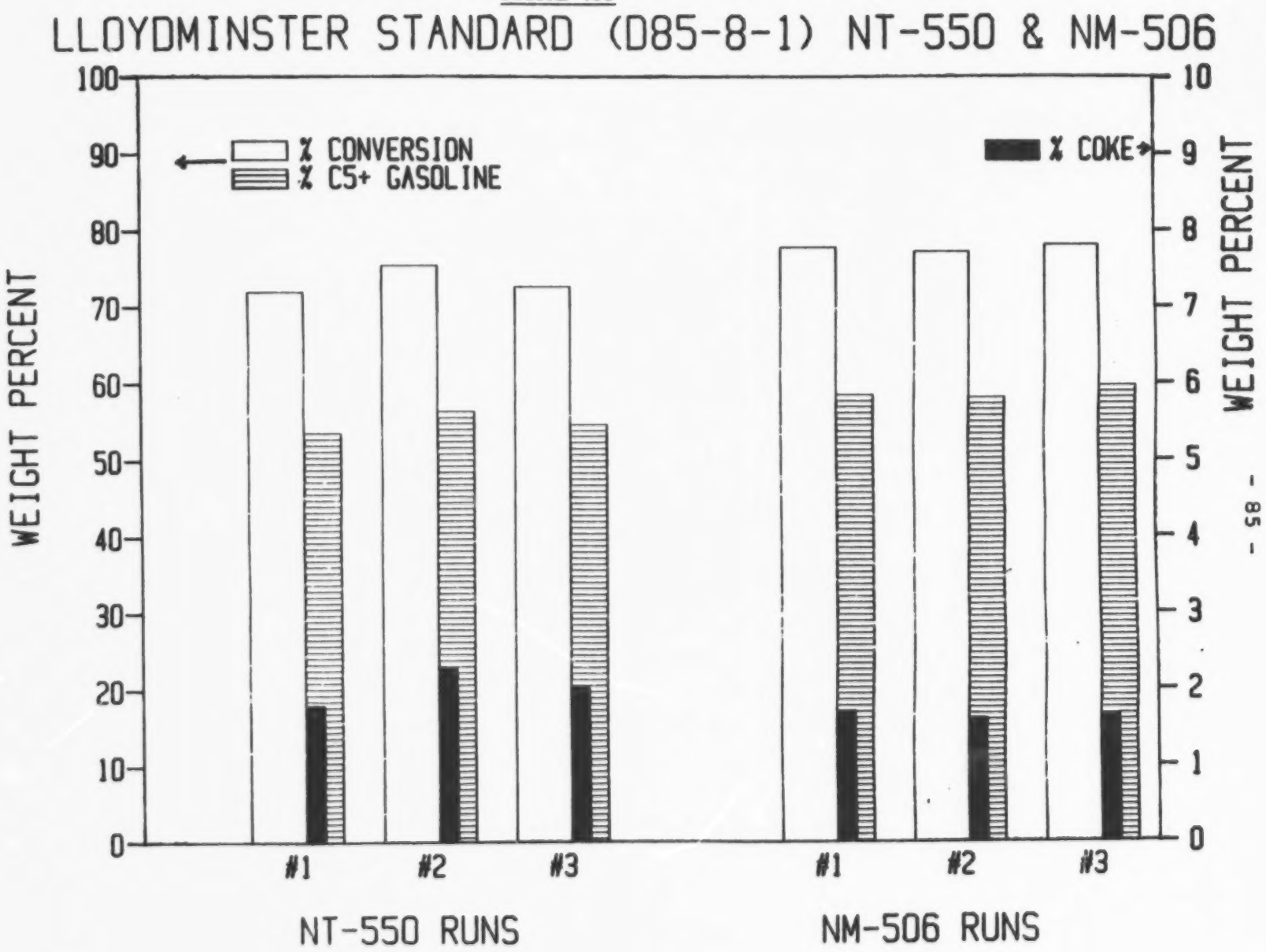

LLOYDMINSTER STANDARD (D85-8-1) NT-550 & NM-506
WEIGHT PERCENT
50
45
40
35
30
25
20
15
10
5
0
% PARAFFINS
% CYCLOPARAFFINS
% MONOAROMATICS
#1
#2
#3
#1
#2
#3
NT-550 RUNS
NM-506 RUNS

FIGURE 16c


LLOYDMINSTER STANDARD (D85-8-1) NT-550 & NM-506
WEIGHT PERCENT
% CONVERSION
% C5+ GASOLINE
% COKE
WEIGHT PERCENT
100
90
80
70
60
50
40
30
20
10
0
10
9
8
7
6
5
4
3
2
1
0
#1
#2
#3
#1
#2
#3
NT-550 RUNS
NM-506 RUNS

CONCLUSIONS

1. Increased in gasoline yield and conversion "can" be obtained by hydrotreating FCCU feedstocks at a moderate temperature (343°C), a high pressure (13.78 MPa) and a moderate space velocity (2 h^{-1}).

2. Hydrogenation conditions of 13.78 MPa, 2 LHSV with NM-506 catalyst gave the most effective desulphurization and denitrogenation, yielded the most gas and gasoline precursors and gave products with the most significant increase in MAT conversion for "all" gas oils tested.

3. For Edmonton Rainbow Zama gas oil hydrogenated with NT-550 catalyst at 13.78 MPa, 2 LHSV, similar conversion and C_5+ gasoline yield with half the hydrogen consumption of NM-506 catalyst was achieved.

4. The removal of sulphur compounds required less hydrogen consumption than the removal of nitrogen compounds.

5. Greater hydrogen consumption occurred with the Ni/Mo catalyst than with the Ni/W catalyst.

6. The Syncrude gas oil did not respond well to hydrogenation. Coker and convention gas oils were far more suitable to hydrogen upgrading.

7. Hydrogenation of gas oils reduced coke make in MAT testing. This may allow the addition of residuum to a hydrogenated FCCU feed and still maintain acceptable coke levels in the fluid catalytic cracking unit.

8. Microactivity test data, obtained at standard conditions show gasoline yields can be increased from 4-9% for Syncrude gas oil and 14-31% for conventional gas (Rainbow-Zama). Hydrogen consumptions required for this, range from 5-245 scf/bbl and 50-481 scf/bbl, respectively. Assuming gasoline is a desired product and hydrogen is relatively cheap, then hydrogenation of FCCU feedstocks should be economically attractive.

RECOMMENDATIONS

1. Hydrogenated gas oils should be evaluated with residua to assess the coprocessing of these materials in the fluid catalytic cracking unit and the optimization of transportation fuel yields from crude oil.

2. All gas oils evaluated in this study with NM-506 should be tested in the MAT at three catalyst to oil ratios. This data can be used to determine the maximum conversion and gasoline yields possible for each hydrogenated product and better estimate its coke selectivity.

3. Alternate feedstocks such as deasphalted oils, should be hydrogenated and evaluated as fluid catalytic cracking unit feedstocks with the microactivity test apparatus. This would be an alternative to direct residuum cracking.

4. Hydrogenation and fluid catalytic cracking of vacuum residua should also be evaluated experimentally.

5. Experimental methods for microactivity test products should be developed which will allow quality parameters such as gasoline octane numbers and light cycle oil cetane numbers to be determined.

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H. Notzl, I. Fisher - Technical Advice

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